

Secondary Formation Products in
Power Plant Plumes

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SECONDARY FORMATION
PRODUCTS IN POWER PLANT PLUMES

by

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ABSTRACT

Source and airborne measurements were made during a two week period (September 24 to October 7, 1979) at the Widows Creek Steam Plant in north-east Alabama. Primary emissions from the flue gas stacks were quantitated including total mass, particle size distribution, $\text{SO}_3/\text{H}_2\text{SO}_4$, SO_2 and NO_x . An instrumented fixed wing aircraft acquired plume data at various altitudes and plume ages. This information was used to study secondary pollutant transformation rates and the contribution of primary emissions to plume concentrations.

Sulfate transformation rates were measured between 4.3 percent-hr⁻¹ and 0.6 percent-hr⁻¹, for a well defined plume at 1.1 hr and 2.2 hr plume ages, respectively. A chemical element balance around the scrubber indicates that as much as 40 percent of the total mass exiting the scrubber was generated from entrained liquor. This accounts for 90 percent of the unit's sulfate emissions. These primary sulfates account for between 4 and 17 percent of the total measured sulfates downwind in the plume.

This report was submitted in partial fulfillment of contract number 68-02-3249 by Radian Corporation under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period August 2, 1979 to October 15, 1980. A data volume describing the results of the experimental measurements is also available.

CONTENTS

Abstract	iii
Figures	vi
Tables	vii
1. Introduction	1
2. Conclusions and Recommendations	4
3. Experimental Description	7
Flue Gas Sampling	7
Process Data and Sample Collection	12
Airborne Measurements	14
Chemical Analysis of Samples	16
Quality Assurance	21
4. Experimental Results	24
5. Discussion of Results	37
Source Characterization	37
Plume Characterization	49
Comparison with Other Studies	67
References	68

FIGURES

<u>Number</u>		<u>Page</u>
1-1	Schematic of TVA's Widows Creek Power Plant	3
3-1	Modified EPA Method 5 Total Particulate Sampling Train	8
3-2	SO ₂ •SO ₃ /H ₂ SO ₄ Sampling Train	11
3-3	Modular Gas Phase Sampling and Analysis System	13
3-4	Flow Diagram of the Calibration System Used to Perform Sulfur Dioxide, Nitric Oxide, Nitrogen Dioxide, and Oxygen Audits	23
5-1	Particle Size Distribution for Unit 7	40
5-2	Particle Size Distribution for Unit 8	41
5-3	Particle Size Distribution for Duct 8B	43
5-4	Particle Penetration Curve	45
5-5	Approach for Measuring Pollutant Transformation Rate	50
5-6	Mapped Flight Plan for Flight 5	55
5-7	Pollutant Profiles at 16 km Downwind during Flight 5, Penetration #2	57
5-8	Pollutant Profiles at 32 km Downwind during Flight 5, Penetration #14	58
5-9	CNC Contour for Flight #5, 16 km Downwind	59
5-10	Contour Plots for Flight #5, 16 km Downwind for SO ₂	60
5-11	Contour Plots for Flight #5, 16 km Downwind for NO _x	60
5-12	Contour Plots for Flight #5, 32 km Downwind for SO ₂	62
5-13	Contour Plots for Flight #5, 32 km Downwind for O ₃	62
5-14	Differential Number (dN/dbg Dp), Surface (dS/d log Dp) and Volume (dV/d log Dp) Distributions Measured during Flight 5 at 16 km Downwind	64
5-15	Differential Number (dN/dbg Dp), Surface (dS/d log Dp) and Volume (dV/d log Dp) distributions measured during Flight 5 at 32 km Downwind	65

TABLES

<u>Number</u>		<u>Page</u>
3-1	Airborne Monitoring Systems	15
3-2	Analysis of Quartz Fiber Filter Sections	17
3-3	IC Instrument Operating Conditions for Analysis of Quartz Filter Leachates	17
3-4	ICP Instrument Description and Operating Conditions for Trace Element Analysis	18
3-5	Mist Samples Collected	19
3-6	IC Instrument Operating Conditions for Analysis of H ₂ SO ₄ Mist Samples	19
3-7	IC Instrument Operating Conditions for Analysis of Scrubber Samples	20
3-8	IC Instrument Operating Conditions for Analysis of Tandem Filter Leachates	21
4-1	Summary of Source Characterization Data TVA Widows Creek Power Plant, October 1979	25
4-2	Summary of Conditions and Results of Modified EPA-5 Sampling	26
4-3	Flue Gas Concentrations (and Percent of Particulate Loading) for Certain Ions (IC) and Elements (ICP) by Method EPA-5*	27
4-4	Synopsis of Andersen Impactor Results	28
4-5	Controlled Condensation Train Conditions and Data	29
4-6	Instrumental Gas Analysis Results	30
4-7	Summary of Boiler Load, SO ₂ Levels, and Opacity Data	31
4-8	Summary of Fuel and Scrubber Data	32
4-9	Summary of Aircraft Flights	33
4-10	Summary of Mean Values of Several Composited Plume Penetration Flights and Upwind Spirals	34
4-11	Plume and Atmospheric Background Species Concentrations	35
4-12	Results of Quality Assurance Audits, Widows Creek, October 1979	36

TABLES (Continued)

<u>Number</u>		<u>Page</u>
5-1	Mass Emissions (kg/hr) from Units 1-6, 7 and 8 at the Widows Creek Steam Plant	38
5-2	Distribution of Inhalable and Respirable Particle Mass	42
5-3	Mass Balances Across SO ₂ Scrubber (from EPA Method 5 Filters) (g/min)	47
5-4	Calculated Mass Flows out of Scrubber (Best Regression Values)	48
5-5	Calculated Sulfate Transformation Rates during the Widows Creek Plume Study	51
5-6	Meteorological Data during Flight #5	54
5-7	Summary of Parameters Measured During Upwind Spiral Flight 5	56
5-8	Summary of Flight 5 Data by Filter Times	63
5-9	Particle Data from Flight 5	66

SECTION 1

INTRODUCTION

Under contract to the Environmental Protection Agency (EPA), Radian Corporation conducted a field measurements program to determine the extent and mechanisms of secondary pollutant formation in scrubbed and unscrubbed power plant plumes. The major pollutants of interest were:

- nitrogen oxides,
- sulfur oxides and
- their respective secondary products (including HNO_3 , NO_3 , H_2SO_4 , HSO_4 and SO_4).

The study required an accurate characterization of the primary emissions from the power plant flue gas stacks and the identity, concentration and spatial distribution of the primary and secondary gases and aerosols formed in the plume as it dispersed from the stack. An instrumented fixed wing aircraft was used to acquire plume data at various altitudes and plume ages (distances downwind). During these measurements the boilers and control devices were monitored for steady state process operation. By comparing the concentrations of various species as the plume dispersed and aged, transformation processes and rates were studied. To date, the literature lacks data with concurrent source (primary) and downwind (secondary) pollutant measurements. In fact, primary sulfate data, particularly from scrubbed emissions, are scarce (1).

The sampling phase of this program was carried out during a two week period (September 24 to October 7, 1979) at the Widows Creek Steam Plant, located in northeast Alabama, 20 miles northeast of Scottsboro, Alabama, and 30 miles west-southwest of Chattanooga, Tennessee. It is operated by the Tennessee Valley Authority (TVA). The site is situated on the northeast bank of the Gunterville Reservoir of the Tennessee River which flows south-westwardly through the area. The terrain around the plant consists of rolling hills within the 3-mile wide river valley bounded about 3 miles to the northwest by the Cumberland Plateau 800 to 1,000 feet above plant grade and about 1 mile to the southeast by the Sand Mountain escarpment, rising 950 to 1,000 feet above plant grade.

The plant has six wall-fired, 135-MW boilers (Units 1-6) which are ducted into a single 1,000-foot stack. Two additional tangentially fired 557-MW boilers (Units 7 and 8) are each ducted to individual 500-foot stacks. Each unit, with the exception of Unit 7, is equipped with an electrostatic precipitator with a design efficiency in excess of 99.5 percent for fly ash collection. The precipitator on Unit 7 has a design efficiency of 90 percent. Ammonia (~10 ppm) is injected into the flue gas to enhance precipitator efficiency for this unit. A limestone wet scrubber has been retrofitted downstream of the electrostatic precipitator on Unit 8; the scrubber has a design removal efficiency of 80 percent for sulfur dioxide (SO_2). Since there are different pollutant removal systems for each flue gas stream, different blends of coal are usually fired in Units 1-6, 7 and 8. Typically, Unit 8 with the SO_2 scrubber will use a higher sulfur coal blend. This information is presented schematically in Figure 1-1.

During the field study, 30.2 hours of aircraft sampling were performed during 12 missions. Airborne pollutant flux measurements were made from 2-15 miles downwind of the plant. A total of 27 high volume (hivol) and 31 tandem filter aerosol samples were collected for subsequent chemical analysis, and over 60 bag samples were obtained and analyzed for particle size distribution information. Concurrent with these flights, source characterization measurements were made on the flue gas from the unit boilers including:

- eight modified EPA Method 5 runs,
- eight in-stack cascade impactor runs,
- eight controlled condensation $\text{H}_2\text{SO}_4/\text{SO}_2$ runs,
- over 14 hours of continuous SO_2 , NO/NO_x , O_2 monitoring and
- collection of scrubber slurry and coal samples.

An independent quality assurance audit was performed during the field program on both aircraft and source sampling instrumentation.

The primary purpose of this report is to present the results and findings of the study, which are summarized in Section 2. The experimental protocol is described briefly in Section 3; a more detailed description is given in the Field Sampling Technical Note (2) available from Radian Corporation. The data obtained during this field program are summarized in Section 4. All the data are on 9-track magnetic tape and in the Data Volume (3), also available from Radian. Section 5 presents a discussion and interpretation of the results.

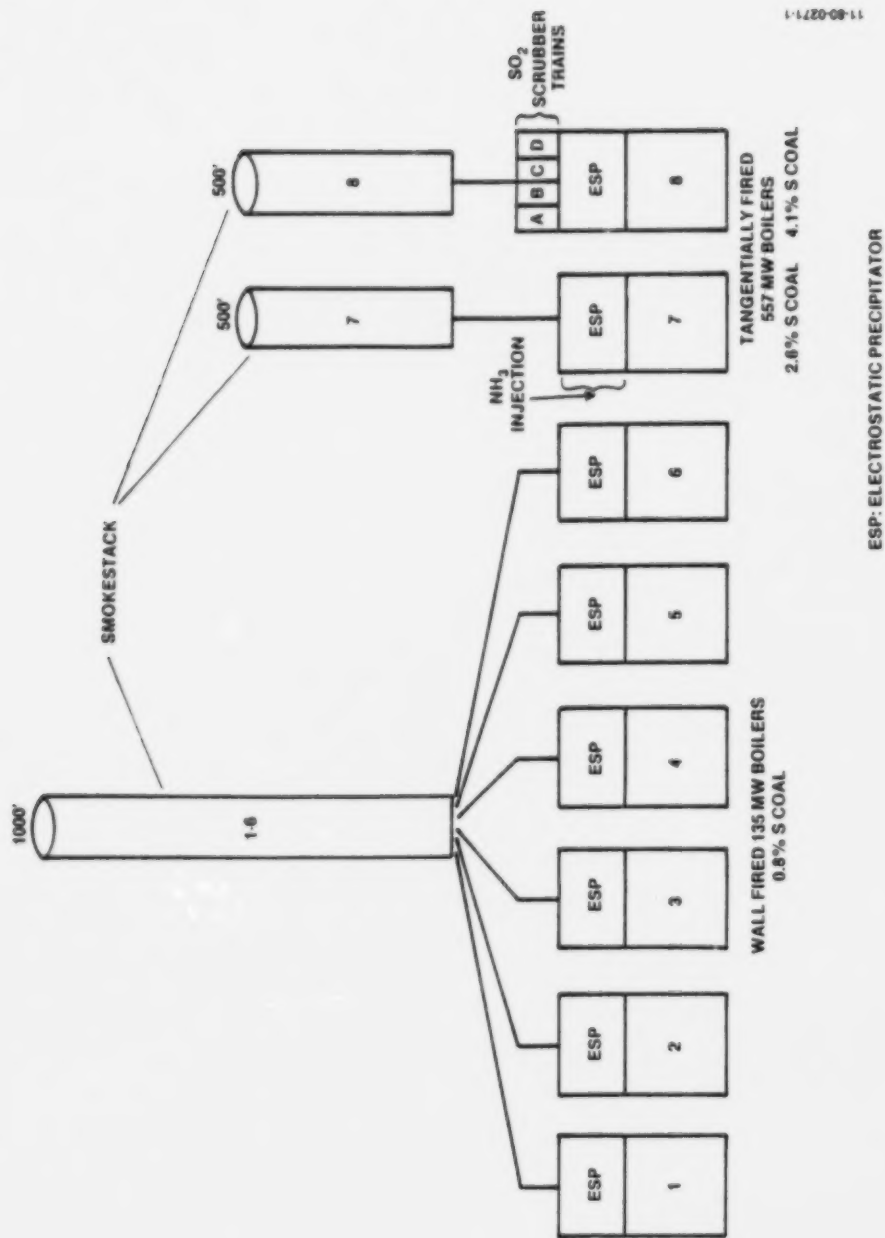


Figure 1-1. Schematic of TVA's Widows Creek Power Plant

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The primary findings and conclusions from this study are presented below.

- The tandem venturi scrubber used at the Widows Creek Steam Plant besides being an effective flue gas desulfurization (FGD) device (>90 percent removal), provided a high degree of particulate control (99.8 percent by mass) during this study (October 1979). Collection by this control device was much less for particles smaller than 2 μm in diameter than for larger particles.
- As a result of the particle collection characteristics of the scrubber, the particulate emissions from Unit 8 exhibit a higher mass fraction of respirable particles (0.5) than from unscrubbed Unit 7 (0.1). However, in terms of absolute respirable mass emissions, Unit 8 is an order of magnitude less than Unit 7.
- Units 1-6 NO_x emission rate was a nominal 50 percent greater than Units 7 or 8. This may be attributed to the fact that Units 1-6 are wall-fired, and Units 7 and 8 are tangentially-fired.
- The scrubber tested did not significantly reduce $\text{SO}_3/\text{H}_2\text{SO}_4$ present in the flue gas.
- A chemical element balance (CEB) around the Unit 8 scrubber shows that 40 percent of the total mass exiting the scrubber is generated from entrained liquor. This accounts for 90 percent of the Unit 8 sulfate emissions.
- Sulfates emitted directly from Units 1-6, 7 and 8 account for between 4 percent and 17 percent of the total measured sulfates downwind in the plume.

- Sulfate transformation rates were measured between 4.3 %/hr and 0.6 %/hr, for a well defined plume at 1.1 hr and 2.2 hr plume ages, respectively. Corrections for primary sulfate emissions were not significant.
- Nitrate transformation rates could not be measured directly, because plume concentration levels were not significantly above filter and/or ambient background levels. Other measurements suggest that the rate is greater than that measured for sulfate, but less than 12 percent-hr⁻¹ (lower detectable rate).
- Aerosol measurements suggest that the primary mechanism for secondary aerosol formation downwind in the plume is homogeneous nucleation.

RECOMMENDATIONS

As a result of the work performed during this program, recommendations can be made in two areas: (1) development and/or refinement of sampling and analytical techniques (2) considerations when selecting a site for plume chemistry studies.

Airborne integrated sampling and analysis techniques are limited to the degree of spatial and temporal resolution they can provide by their analytical limits of detection. As an example, during this study and similar airborne programs (4,5) nitrate and/or HNO₃ levels in the plume have not been significantly above the sampling and analytical detection limits. Areas to investigate include:

- The use of high volume sample collection. This would require filtration media which would not result in high pressure drops at high flow rates.
- Filtration material with low, consistent background levels.
- Ultimately, development of dependable real time continuous analyzers, especially for SO₄²⁻ and NO₃⁻.

Selection of a site suited for plume chemistry measurements requires consideration of a number of parameters. At a minimum, these should include the following:

- A good history of unit availability.
- Constant load operation, in contrast to units which respond to distribution grid requirements.

- Stable fuel source, preferably the same for all units.
- Sampling period which historically has persistent winds and meteorological conditions that favor stable plume formation.
- Local terrain that will have little effect on plume dispersion, chemistry and flight paths.

SECTION 3

EXPERIMENTAL DESCRIPTION

One of the major objectives of this study is to determine the extent of secondary pollutant formation in power plant plumes. This requires an accurate characterization of the primary emissions, i.e., gas, liquids and solids emitted directly by the source. Previous studies (e.g. 6,7) of plume chemistry often have not had coincident primary emissions data. To identify secondary pollutants, i.e., pollutants formed after being emitted by the source, sampling was conducted in the plume at various plume travel times. By comparing the composition of aerosol samples obtained as the plume aged, the formation of aerosols could be determined.

One of the unique features at this study site is the opportunity to study scrubbed and unscrubbed plumes. Since the two of these plume (Units 7 and 8) often intermingle at this site, it is possible that secondary pollutant formation in mixed plumes can be studied. For this reason, most of the source sampling was conducted on Units 7 and 8; unscrubbed and scrubbed units, respectively.

FLUE GAS SAMPLING

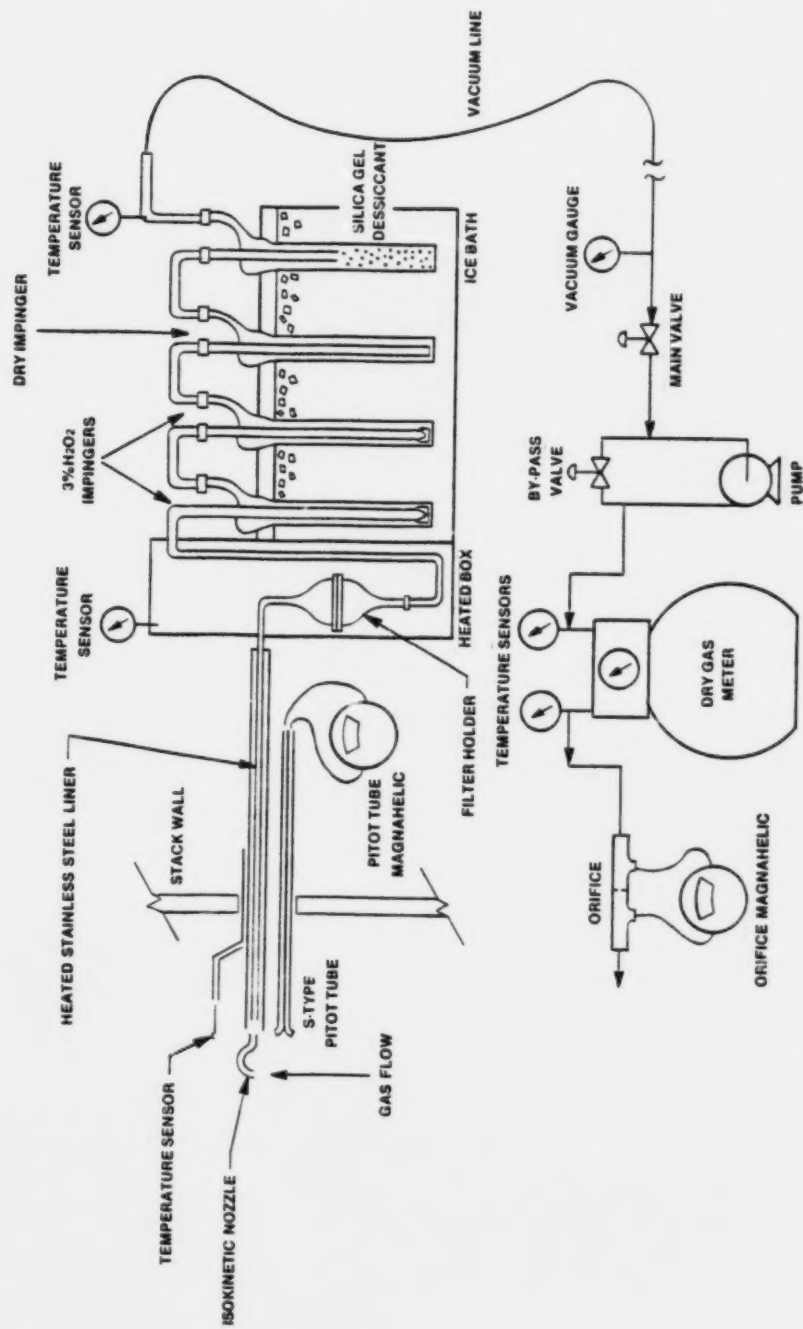
To meet the objectives of the project, a flue gas sampling plan was developed to measure the following parameters:

- total particulate mass and composition,
- particle size distribution,
- the SO_2/SO_3 /sulfuric acid mist concentration and
- gas phase composition.

Also, samples of scrubber slurry were taken. A brief description of each sampling and analytical procedure is given below; complete details are available elsewhere (2).

Total Particulate Mass

The total particulate mass grain loading was measured at the exit of the two stacks servicing Units 7 and 8 and at the Unit 8B train scrubber inlet. Unit 8 had four scrubber trains, each handling nominally 25 percent of the flue gas. A modified version (see Figure 3-1) of the sampling train specified in EPA Method 5 (8) was used to isokinetically collect the



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Figure 3-1. Modified EPA Method 5 Total Particulate Sampling Train

particulate samples. The sampling train consisted of:

- a stainless steel gooseneck nozzle and heat-traced glass lined probe,
- a heated enclosure housing a filter for particulate removal,
- an impinger train for moisture and SO_2/SO_3 collection and
- a pump and dry gas meter for flow control and metering.

Preliminary data to determine the velocity and temperature profiles, molecular weights and moisture content of the flue gas were collected using techniques specified in EPA Methods 1 through 4 (8).

Quartz filters (Gelman® Micro-Quartz Glass Fiber Filters) were pre-treated to minimize artifact formation. Filters were submersed in 0.1N phosphoric acid overnight, rinsed with distilled water three times and dried at 550°F overnight. The total weight of the particulate catch from the nozzle and probe wash and filter catch was used to determine the particulate mass loading. The filters were stored in petri dishes and kept for subsequent sulfate, nitrate and trace metal analysis. Moisture was condensed and measured in a series of impingers, and the dry gas volume was metered. The SO_2/SO_3 collected as sulfate in the three percent H_2O_2 impinger solutions was quantified by ion chromatography as described below.

Particle Size Distribution

Flue gas particle size distributions were measured at the exit of the stacks servicing Units 7 and 8 and at the Unit 8B train scrubber module inlet. An Andersen Mark III® cascade impactor was used in performing the size distribution measurements (9). Particles present in the gas stream were classified with respect to their aerodynamic size and impacted on a series of collection surfaces. This process separates the particles into nine size fractions.

Glass fiber (Reeves Angel 934AH) collection substrates, pre-treated with phosphoric acid as described above to reduce any interaction with SO_2 , were used as impaction substrates. Impactor sampling was performed isokinetically at a single point of average velocity in the gas stream. Operation of the Andersen impactor requires that the flow rate through the impactor be kept constant. This requirement eliminates the possibility of adjusting the flow rate if variations in gas velocity occur. An electrical heat tape was used to elevate the temperature of the impactor body during sampling on the Unit 8 stack. The elevated temperature was required to eliminate the possible presence of condensed moisture in the flue gas. After sampling, the impactor was unloaded and the substrates were reweighed. All substrates were weighed using a Cahn Electrobalance®. Filter weight gains were then used to calculate the particle size distribution.

Sulfuric Acid Mist ($\text{SO}_3/\text{H}_2\text{SO}_4$)

A controlled condensation sampling technique (10) was used in the qualitative separation and quantitative collection of $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 present in the flue gas on Stacks 7 and 8 and at the Unit 8B train inlet. The sampling train (Figure 3-2) consists of the following components:

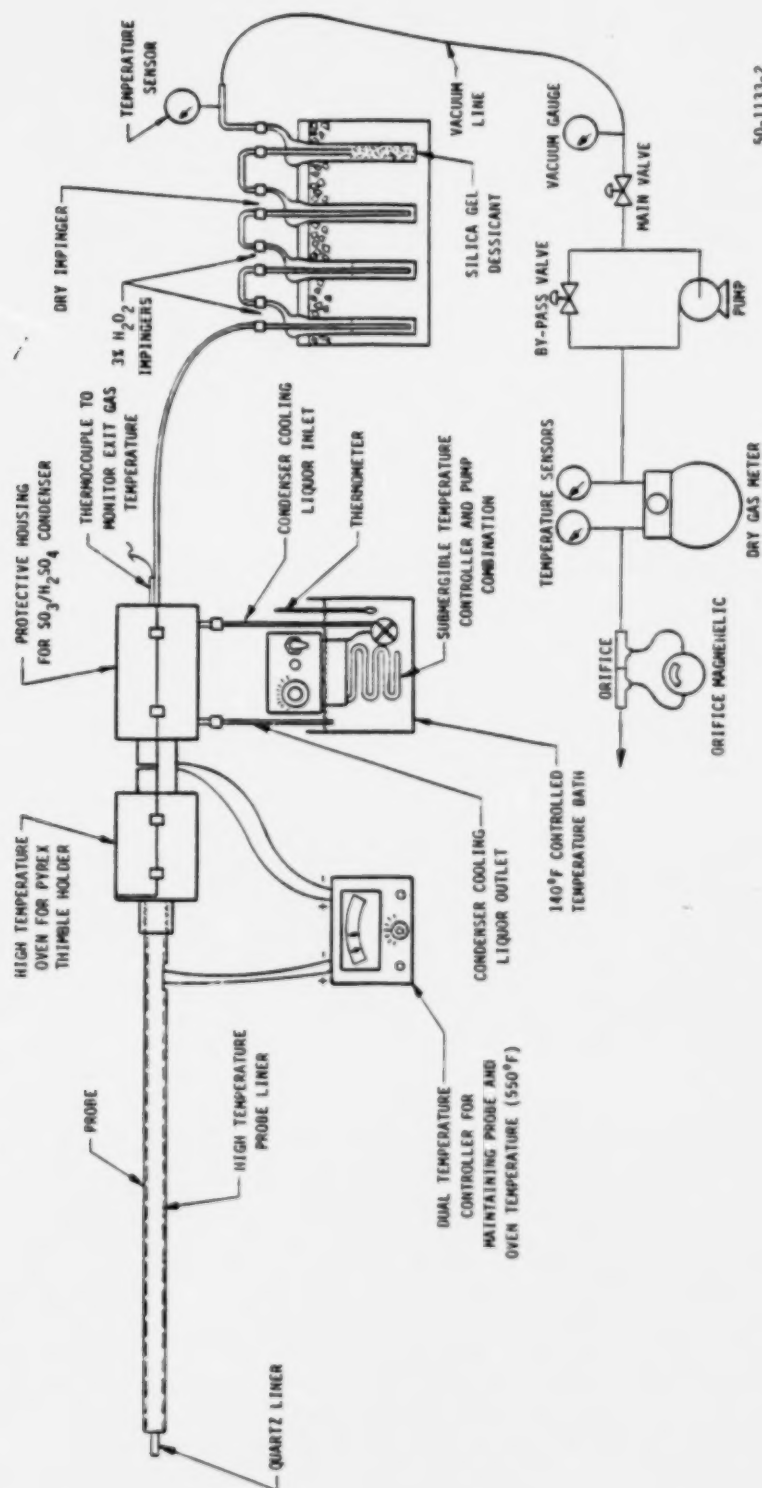
- a high temperature (550°F) quartz-lined probe,
- a high temperature (550°F) quartz filter holder for particulate removal,
- a temperature controlled (140°F) condenser for collection of $\text{SO}_3/\text{H}_2\text{SO}_4$,
- an impinger train for SO_2 collection and moisture removal, and
- a pump and dry gas meter for controlling and metering sample flow.

The 13.5 foot probe constructed for this study allowed traversing of each stack quadrant and the inlet duct. The particulate matter was removed by the hot filter while the SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ (gas and/or vapor) passed through. SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ exiting the filter holder then entered a modified Graham condenser that was housed in an insulated cylindrical enclosure. $\text{SO}_3/\text{H}_2\text{SO}_4$ was removed from the gas stream by means of condensation in the condenser that was maintained at 140°F to 160°F . SO_2 and moisture present in the gas exiting the condenser are collected in a series of impingers similar in design and content to the impingers used with the EPA-6 method sampling train (8).

During sample collection, a proportional sampling technique was used to collect a representative gas sample. Based on this technique, the volume of gas collected at each sampling point is proportional to the total gas flow rate at that point. The sampling rate was maintained at 0.4 cfm (nominal) and the sampling time varied at each point. After sampling was completed the filter holder and condenser were removed from the system and taken to the on-site laboratory. The quartz filter was removed from the filter holder and stored in a petri dish. The condenser unit was then rinsed with a known volume of deionized water to remove any sulfate present. The impingers were used for SO_2 and moisture determination as described in EPA Method 6.

Gas Phase Composition

Preliminary gas phase analysis (CO_2 and O_2) was performed during velocity profile determinations on Units 7 and 8 stacks by measuring the volume of the gas (CO_2 or O_2) selectively absorbed by a Fyrite® sampling train. The balance of the gas composition was assigned as nitrogen for the purpose of calculating a flue gas molecular weight.



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Figure 3-2. SO₂-SO₃/H₂SO₄ Sampling Train

In addition, a modular acquisition, conditioning and instrumental analysis system was used during this project to continuously and simultaneously measure the SO_2 , NO/NO_2 , and O_2 content of the flue gas. Measurements were made from a single port on stacks 7 and 8 and the 1-6 stack. Three point traverses were made to determine if major concentration gradients existed.

The modular system, graphically illustrated in Figure 3-3, consists of (1) a heat-traced probe and umbilical, (2) a heated gas conditioning system, and (3) two rack mounted sets of instruments, recorders, and required plumbing. The heated probe and umbilical (180°F - 210°F) were used to transport the sample from the stack without allowing moisture to condense prior to the conditioning unit. In the heated (180°F - 210°F) conditioning unit, particulate matter and water are removed.

A Bendix Model 8201 NO_x analyzer was used to measure the NO and NO_2 concentration present in the sample gas. The method analyses the light emitted from the chemiluminescent reaction of NO and ozone.

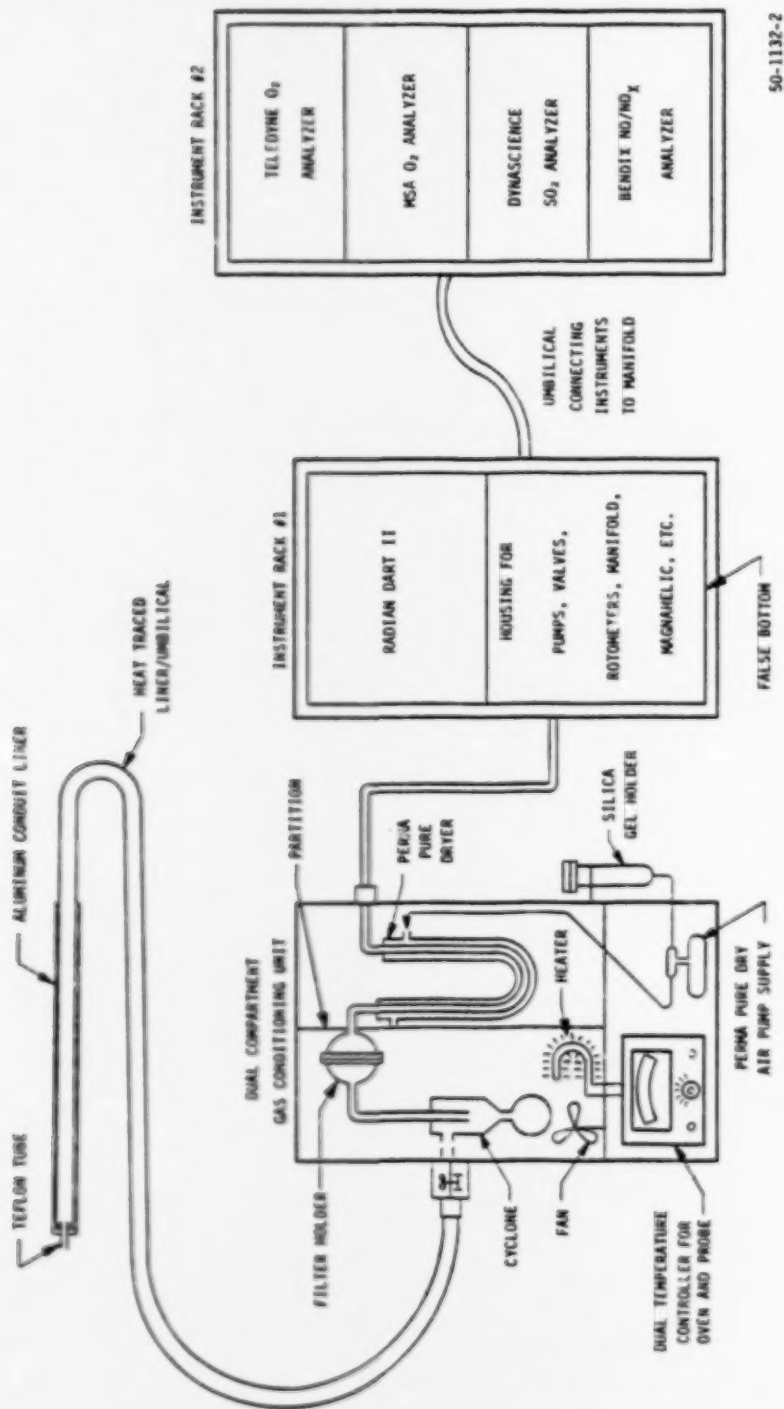
A Dynascience Model P300 SO_2 analyzer was used to measure the SO_2 concentration of the flue gas. Sulfur dioxide present in the flue gas diffuses through a membrane and thin electrolytic layer where the SO_2 is then absorbed by a sensing electrode. An electrochemical transducer generates an electrical current that is directly proportional to the partial pressure of the SO_2 gas.

A Teledyne Model 320P-4 analyzer and a MSA Model 803P analyzer were both used to monitor the oxygen present in the flue gas. The MSA unit was used to continuously monitor the O_2 concentration while the Teledyne unit was used to spot check the MSA readings. Both the MSA and Teledyne units use a fuel cell to directly analyze the oxygen present in a gas stream.

Before sampling, the instruments were calibrated in the on-site laboratory using NBS traceable gas mixtures. After sampling was completed at each location, the instruments were taken back to the laboratory where each instrument's span and zero were checked.

PROCESS DATA AND SAMPLE COLLECTION

A simultaneous, continuous characterization of the SO_2 and particulate emission rate from all three stacks was not within the scope of this project. Therefore, to determine if these emission rates varied significantly during aircraft sampling periods, data from the power plant's process and air pollution monitoring equipment were obtained. Certain boiler and turbine operating parameters as well as certain environmental emission rates (SO_2 and opacity) are routinely monitored at the Widows Creek Steam Plant by TVA. Control room operators manually record important operational data (typically once an hour) onto log sheets in order to keep a running tally of both boiler and turbine operation. Copies of these



50-1132-2

Figure 3-3. Modular Gas Phase Sampling and Analysis System

control room log sheets for Units 1 through 8 were obtained from plant personnel during the period of September 29 through October 7, 1979. Radian personnel also visited the Units 7 and 8 control room on a frequent basis to keep abreast of unit operations during the sampling.

In addition to these data, samples were obtained of the fuel burned and of the scrubber liquor. Three types or mixtures of coal are used at the Widows Creek Steam Plant (usually in different boilers 1-6, 7 or 8). A continuous automated sampling system is used at Widows Creek to collect a 24-hour composite of the coal prior to storage in the silos for use the next day. Plant personnel routinely collect these coal samples in order to determine the heating value, moisture, and sulfur content of the coal along with other chemical analysis. A portion of this sample was provided to Radian. The various coal samples were collected so ultimate and proximate analysis as well as certain trace metal analysis could be performed if necessary. Scrubber slurry samples were collected twice daily on the Unit 8B scrubber train when Unit 8 was in operation. The sample was filtered as it was withdrawn. Temperature and pH measurements were made during sampling. The filtered solids and the dissolved solids were dried and stored for future analysis.

AIRBORNE MEASUREMENTS

Under a subcontract, Pennsylvania State University (PSU) conducted airborne sampling with the assistance of Radian personnel. PSU's Aerocommander 680E fixed wing aircraft (11) contained the instruments listed in Table 3-1 and a data acquisition system designed and built by PSU. All data channels were polled twice a second and the instrument voltages stored on magnetic tape. The resulting data tape was processed later at PSU's computing facilities in State College, Pennsylvania.

A 0.1 m³ (nominal) bag was filled during plume penetration using a ram jet induction manifold for aerosol size distribution analysis. The size distributions were determined by sampling the air in the bag with the electrical aerosol analyzer immediately upon leaving the plume. The bag was then flushed several times with clean ambient air before obtaining another plume sample. The bag was pretreated to minimize wall losses due to electrical charge by rinsing the bag with a dilute soap solution and allowing it to air dry.

Two types of filters were used to obtain aerosol samples for subsequent chemical analysis. Pretreated quartz filters (Gelman® Micro-Quartz Glass Fiber Filters) were used with a high volume air sampler to obtain aerosol samples for sulfate and cation analysis. A tandem filter packet (12) was used to sample for nitrates and nitric acid. The first filter was untreated Teflon® filter to capture nitrates followed by a nylon filter (Ghid®) to collect nitric acid. Aerosol samples were obtained with this tandem filter packet using a diaphragm pump. Filter sampling was conducted while the aircraft was in the plume (based on observed levels of SO₂ and/or CNC), or while making an upwind spiral.

TABLE 3-1. AIRBORNE MONITORING SYSTEMS

Parameter	Principle	Manufacturer	Model
<u>Aerosols</u>			
Condensation nuclei	Cloud chamber	Environment One	RICH 100
Particle size distribution (0.01 - 1 μ m)	Electrical mobility	Thermo Systems	Electrical Aerosol Analyzer 3030
Light scattering coefficient	Integrating nephelometer	Meteorological Research, Inc.	1550B
<u>Gases</u>			
SO ₂	Pulsed fluorescence	Thermal Electron	43
O ₃	Chemiluminescence	McLoy	OA350
NO/NO _x	Chemiluminescence	Thermal Electron	14D-E
<u>Weather</u>			
Static pressure	Capacitance sensor	Rosemont Engr.	830 RA
Temperature	Platinum resistor	Rosemont Engr.	102DL24
Dew point	Cooled mirror thermometer	Cambridge Systems	137-C3
<u>Position</u>			
Ground speed	Doppler Radar	Singer General Precision	CPK-1000
Drift angle	Doppler Radar	Singer General Precision	CPK-100
Navigation	VOR/DME	Foster Air Data System	RNAV 511

CHEMICAL ANALYSIS OF SAMPLES

Several samples obtained during this program were analyzed for various anions and cations. The analytical procedures used are described below.

Quartz Fiber Filter Handling and Analysis

Quartz fiber filters were used to collect EPA-5 type samples during source testing at Widows Creek and to collect particulate material in the plumes. Filters from both uses were handled similarly; both filters were weighed on site to measure total weight gain. Then all quartz filters were divided into four portions of approximately equal size and weighed. Individual portions were transferred into separate 60 ml polypropylene bottles and sealed for transport to and analysis in Radian's Austin laboratories. Table 3-2 lists the use for which various sections were intended.

Source and plume filter sections were leached in a similar manner. Fifteen ml of CO₂-free deionized water (freshly prepared) was pipetted into each bottle containing a plume filter section. Forty ml of deionized water was pipetted into each bottle containing a stack filter section. All bottles were shaken for one hour on a wrist action mechanical shaker, then placed in an ultrasonic bath for one-half hour.

Ion chromatography (IC) analysis was performed on each sample as soon as possible (typically within one or two hours, often less) after leaching. A Dionex® Model 10 ion chromatograph equipped with 3 x 500 mm separator column was used for all analyses. Instrument conditions are listed in Table 3-3.

Standard solutions containing the anions of interest that covered the range of concentrations found in samples were prepared from 0.1M stock solutions. The stock solutions were made from Baker Dilut-it® certified concentrates. New calibration curves were prepared on a daily basis, and standards were injected periodically throughout the operating day. At least once per day, a sample was analyzed in duplicate to characterize reproducibility. A quality control sample was analyzed on a daily basis. Blank filters (2 for EPA Method 5, 6 for ambient aerosol samples) were handled and analyzed according to the same procedures used for sample filters.

Source and plume quartz filter sections were digested for trace element analysis in an identical manner. The filter sections were placed in 100 ml Teflon® beakers. Twenty-five ml of Ultrex® HNO₃ was added, the beakers were covered with Teflon® watch glasses, and heated at 50°C for 10 hours. After cooling, 10 ml HNO₃, 5 ml Ultrex® HCl, and 5 ml Ultrex® HF were added. Beakers were again heated for 10 hours at 50°C, then boiled for one hour. After cooling, 5 ml Ultrex® HClO₄ were added, then the beakers were heated till white fumes (HClO₄) appeared. After cooling, the sides of beakers were washed down with about 2 ml deionized water, then evaporated to dryness. After cooling 2 ml of HNO₃ and 50 ml deionized water were added. Beakers were warmed until solutions were clear, cooled and diluted to 100 ml.

TABLE 3-2. ANALYSIS OF QUARTZ FIBER FILTER SECTIONS

Section Identification	Used For
A	Digestion and ICP (trace element) analysis
B	H ₂ O leach and Dionex analysis
C	Benzaldehyde extraction-sulfuric acid analyses
D	Spare

TABLE 3-3. IC INSTRUMENT OPERATING CONDITIONS FOR ANALYSIS OF QUARTZ FILTER LEACHATES

Parameter	Value
Separator Column	Standard resin, 500 mm x 3 mm
Injection Loop Volume	0.1 ml
Eluent Flow Rate	30% (2.5 ml/minute)
Eluent	3.6 mM NaHCO ₃ /2.88 mM Na ₂ CO ₃
Conductivity Range	3 μ mho

Trace analysis on filter digestions were performed using an inductively coupled argon plasma emission spectrometer (ICP). The ICP combines the use of an emission spectrometer with a radio frequency generated argon plasma source. This provides the ability to analyze samples over wide ranges of concentrations without the need to dilute samples.

The samples are aspirated into the argon plasma which may reach temperatures of 10,000°K. The emitted light is focused onto a grating which diffracts the light. The spectral bands associated with each element are incident upon separate photomultiplier tubes. The system is computer-controlled which allows for simultaneous, multi-element determinations by comparing the current of each photomultiplier tube to the current measured during standardization. The ICP also allows for automatic background correction to adjust for matrix interferences. Instrument description and operating conditions are detailed in Table 3-4. Calibration and quality control procedures were used as described above.

TABLE 3-4. ICP INSTRUMENT DESCRIPTION AND OPERATING CONDITIONS FOR TRACE ELEMENT ANALYSIS

Description	Operating Conditions
Instrument Type	Applied Research Laboratories 34000
Sample Introduction	Coaxial Pneumatic Nebulizer
Argon Flow	1.5 L/min
Instrument Control, Data Manipulation and Storage	DEC VT/100 Terminal DEC Decuriter II Data Systems DSD 210 Diskett Memory System
Spectrometer Interface Language	BASIC
Grating	1920 L/mm Blazed at 300 nm, range 189-461 nm
Entrance, Exit Slits	12 μ m, 50 μ m

Analysis of Sulfuric Acid Mist Train Samples

Table 3-5 lists the samples collected from sulfuric acid mist train runs. All samples were analyzed as collected, except for the filters and glass wool plugs. Filters were leached with 50 ml of CO₂-free deionized water. The leachate was filtered through a standard 47 mm millipore apparatus and sealed until analyzed. Glass wool plugs were placed in 50 ml of CO₂-free deionized water and sealed until analysis.

TABLE 3-5. MIST SAMPLES COLLECTED

Sample Description	Sample Form
Filter Holder Probe Rinse	Liquid
Filter	Filter with Solids
Condenser Rinse	Liquid
Glass Wool Plug	Glass Wool/Liquid
Vacuum Line Wash	Liquid
Impinger 1	Liquid
Impinger 2 and 3	Liquid

All samples were analyzed for sulfate using ion chromatography. A Dionex Model 10 was used for all analyses. Instrument conditions are listed in Table 3-6. Standard solutions for daily calibrations were prepared using Dilut-it® certified concentrates. Quality control samples were analyzed on a daily basis, and 10 percent of the samples were analyzed in duplicate.

TABLE 3-6. IC INSTRUMENT OPERATING CONDITIONS
FOR ANALYSIS OF H₂SO₄ MIST SAMPLES

Instrument	Operating Conditions
Separator Column	Standard Resin 500 mm x 3 mm
Injection Loop Volume	0.1 mL
Eluent Flow Rate	30% (2.5 mL/min)
Eluent	3.0 mM NaHCO ₃ /2.4 mM Na ₂ CO ₃
Conductivity Range	30 µMho

Scrubber Liquid and Solid Samples

Chemical analysis was also performed on both liquid and solid scrubber samples. Filtrates were analyzed directly by both IC analysis and ICP. Solids were digested for IC and ICP analysis.

Solid samples (1.0 g ± 0.1 mg) were dried to 60°C+, ground with a mortar and pestle, and sieved to a diameter less than 75 microns. The sized samples was weighed on an analytical balance and quantitatively transferred to a clean 500 mL volumetric flask. To this was added 250 mL of deionized

water, 2.0 ml of 30 percent H_2O_4 , and a clean Teflon® stirring bar. The flask was tightly stoppered and stirred 10 minutes. Twenty ml of 1M HCl was added and the flask was stirred for an additional 30 minutes with the stopper tightly secured. The stirring bar was removed, and the flask was diluted to volume. The sample was mixed well and approximately 50 ml was filtered through a tared 0.4 μ m millipore filter into a one liter suction flask. The filtrate was swirled in the flask and discarded. The remaining solution was filtered and transferred to a clean polyethylene bottle for storage. The volumetric flask was rinsed with deionized water which was then used to transfer remaining solids onto the filter. The filter was dried for two hours at 60°C and weighed.

Ion chromatograph analysis was used to determine anions of interest in scrubber filtrates and solids. A Dionex Model 10 was used for analysis. Instrument conditions are listed in Table 3-7. Calibration and quality control procedures were used as described previously.

TABLE 3-7. IC INSTRUMENT OPERATING CONDITIONS FOR ANALYSIS OF SCRUBBER SAMPLES

Instrument	Operating Conditions
Separator Column,	Standard Resin, 3 x 500 mm
Injection Loop Volume	0.1 ml
Eluent Flow Rate	30% (2.5 ml/min)
Range	30 μ Mho
Recorder	Linear Model Stripchart, Dual Channel

For ICP analysis, samples of scrubber solids (1.0 g portions) were digested using the standard perchloric acid digestion (PAD) described previously and ICP analysis performed as described for the quartz filters.

Tandem Filters

Tandem filter packets were used during airborne sampling for nitrate and nitric acid analysis. Both filter types in the packet (Teflon® and nylon) were leached in a similar manner. Filters were removed from their petri dishes with Teflon®-coated tweezers and placed in new 30 ml polypropylene bottles. These bottles were pre-rinsed with leachate solution. Into each bottle was pipetted 10.0 ml of leachate solution and sealed immediately. The solution was shaken on a wrist action mechanical shaker for one hour then placed in an ultrasonic bath for 30 minutes.

The leachate solution was identical to the Dionex eluent used for leachate analysis. A solution of 3.0 mM NaHCO_3 , 2.4 mM Na_2CO_3 was prepared and used for both leaching and sample elution.

Tandem filter leachates were analyzed using instrumental ion chromatography. A Dionex Model 10 ion chromatograph equipped with standard anion separator (3 x 500 mm) and suppressor columns were used for all work associated with this project. Table 3-8 lists the operating conditions for tandem filter leachate analysis. Calibration and quality control procedures were identical to those described previously.

TABLE 3-8. IC INSTRUMENT OPERATING CONDITIONS FOR ANALYSIS OF TANDEM FILTER LEACHATES

Parameter	Value
Separator Column	Standard resin, 500 mm x 3 mm
Injection Loop Volume	0.1 ml
Eluent Flow Rate	30% (2.5 ml per minute)
Eluent	3.0 mM NaHCO_3 /2.4 mM Na_2CO_3
Conductivity Range	3.0 μMho

QUALITY ASSURANCE

A multi-faceted program was conducted to control and document data quality. All source sampling equipment including dry gas meters, thermocouples, pressure gauges, orifice meters and pitot tubes were calibrated prior to field use. Daily calibrations of analytical instruments were performed as well as duplicate and blank analyses. In addition, independently prepared audit samples were analyzed. Finally, statistical and engineering analysis of the data was performed to assess the variability and reasonableness of the data.

Multipoint calibration of the instruments in the aircraft was conducted prior to the initial flight and approximately midway through the program. Instrument zeros were also checked during each flight. A log was maintained on each flight which documented the pertinent aspects of the flight. In addition to recording location references, instrument values were recorded at various times from their panel meters to serve as a quality assurance check during validation of the processed data.

Field Audit Procedures

All gas analyzers (aircraft and source), including SO₂, NO_x, O₂, and O₃, were audited by introducing a zero gas and several upscale concentrations through the sample port using a modified Bendix 8861 DA calibrator (see Figure 3-4). These audit points nominally corresponded to 0, 10, 20, 40, 60 and 90 percent of full scale. The SO₂, NO_x, and O₂ analyzers were audited by diluting high concentration gases from cylinders taking care to vent the excess sample to the atmosphere through a "T" arrangement.

When an audit sample was supplied to an analyzer, the analyzer response was allowed to stabilize and the response noted. The indicated response was then converted to a corrected ppm value using the most recent instrument calibration curve. The corrected response was then compared to the audit input and a percent difference calculated using the following equation:

$$\text{Percent Difference} = \frac{(\text{Actual Response, ppm or \%}) - (\text{Audit Input, ppm or \%})}{(\text{Audit Input, ppm or \%})} \times 100 \quad (4-1)$$

Procedures used to audit the SO₂, NO_x, and O₃ analyzers were consistent with the methods described in 40 CFR Part 50.

Due to the high concentration ranges monitored by the stack analyzers, the Bendix calibrator had to be spatially modified to produce the higher concentration gases. Since the Bendix 8861 is designed to audit/calibrate the low ranges normal to ambient monitoring, high source flow capillaries had to be prepared, installed, and calibrated to provide the higher concentrations of SO₂, NO, and NO₂.

Known concentrations of NO₂ were generated by the gas phase reaction of NO with ozone. NO reacts with ozone on a 1:1 basis to form NO₂ and O₂. Therefore, the NO response will drop with the addition of ozone. The concentration of the NO₂ input is calculated by computing the difference between the original NO response and the NO response after the addition of ozone. Five equally spaced NO₂ concentrations were generated by this method. In addition, the analyzer's ability to convert NO₂ to NO was determined.

The Meloy ozone analyzer in the aircraft was also audited with the Bendix 8861 calibrator. The ozone source in the calibrator was calibrated against a primary standard Dasibi UV photometer. Ultraviolet photometry is presently the Federal Reference Method for ozone measurement.

The MSA Oxygen Flue Gas Analyzer was audited by diluting ultra-pure oxygen with prepurified nitrogen. The same Bendix calibrator used for the other audits was used to dilute the oxygen, however, the nitrogen was used as a dilution source.

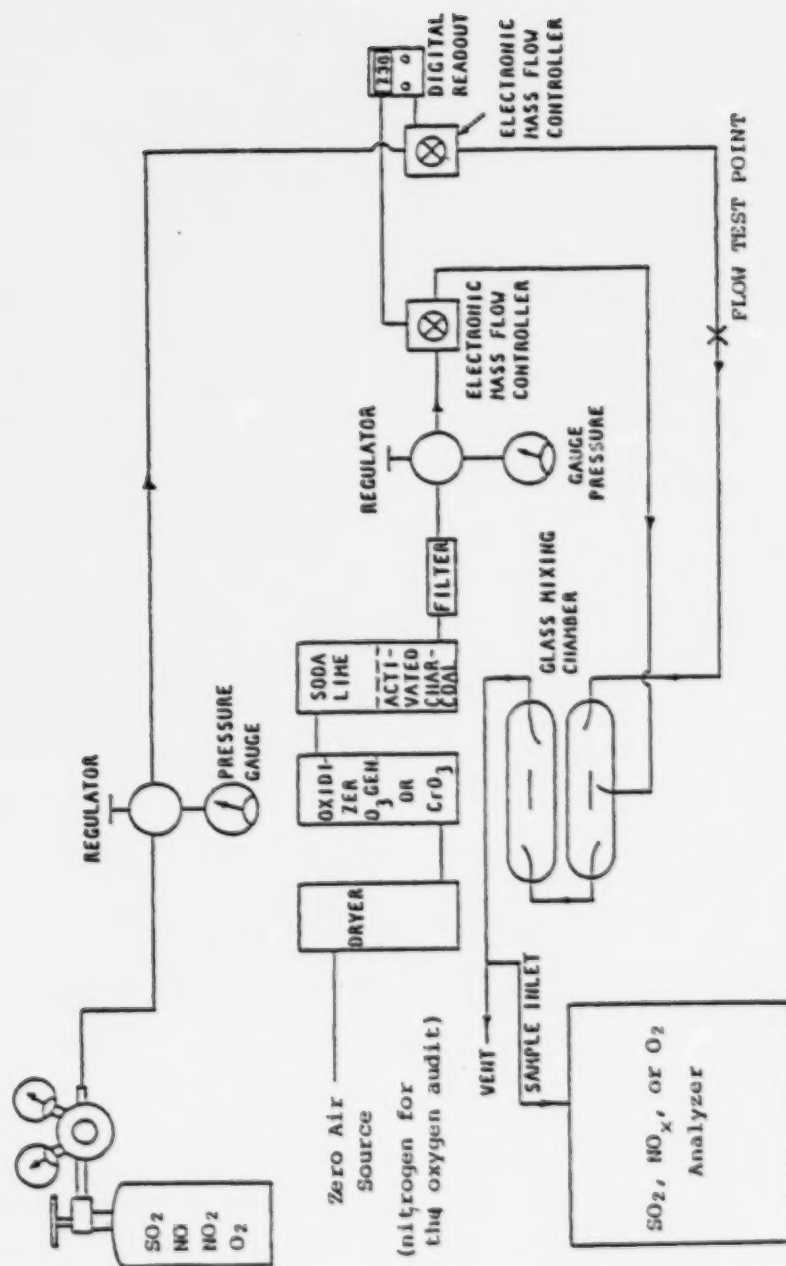


Figure 3-4. Flow diagram of the calibration system used to perform sulfur dioxide, nitric oxide, nitrogen dioxide, and oxygen audits.

SECTION 4

EXPERIMENTAL RESULTS

The results of this two-week sampling effort are summarized here. Raw and processed data are available in the Data Volume (3) and on nine-track magnetic tape. Tables 4-1 through 4-8 summarize the source characterization data obtained by Radian and TVA. Tables 4-9 through 4-11 summarize the results of the airborne measurements. The Data Volume also contains ground level and upper air meteorological data, not summarized here, that were collected by TVA on the airborne sampling days.

The quality assurance audit of the stack and airborne gas monitors indicated that all the instruments were accurate within ± 20 percent of the audit value (see Table 4-12). Occasionally the NO/NO_x instrument in the aircraft produced large short-term values. Average NO/NO_x concentrations from this instrument should be discounted because of these spurious values. Reproducibility of chemical composition analyses was good (± 10 percent). However, the large blank values for sodium on the quartz filters may have masked the presence of sodium collected on the filters.

TABLE 4-1. SUMMARY OF SOURCE CHARACTERIZATION DATA TVA WIDOWS CREEK POWER PLANT, OCTOBER 1979

		Units 1-6 (Unscrubbed)	Unit 7 (Unscrubbed)	Unit 8 (Scrubbed)	Unit 8B Inlet*
<u>Modified EPA Method 5</u>					
Particulates (gm/m ³)	Mean	NM	2.30	0.015	5.61
	Range	NM	1.52-3.20	0.009-0.021	N
SO ₂ + SO ₃ (ppm)	Mean	NM	1787	192	2051
	Range	NM	1663-1882	113-270	N
<u>Chemical Composition</u> (% of each sample's total mass)					
F ⁻	Mean	NM	0.004	<0.001	0.003
	Range	NM	0.002-0.007	--	N
Cl ⁻	Mean	NM	0.002	<0.005	0.028
	Range	NM	ND-0.004	--	N
SO ₄ ²⁻	Mean	NM	0.062	25.45	0.812
	Range	NM	0.370-0.933	25.70-26.20	N
Na	Mean	NM	0.072	ND	0.115
	Range	NM	0.034-0.753	--	N
Ca	Mean	NM	0.621	5.40	0.660
	Range	NM	0.268-1.208	3.49-7.32	N
Al	Mean	NM	2.63	4.04	2.28
	Range	NM	1.54-4.63	3.95-4.13	N
Mg	Mean	NM	0.153	0.413	0.106
	Range	NM	0.091-0.318	0.349-0.478	N
Ti	Mean	NM	0.122	0.426	0.136
	Range	NM	0.075-0.247	0.400-0.451	N
<u>Particle Size Distribution</u> (% of Mass less than 2 μ m)	Mean	NM	10.6	37.0	10.9
	Range	NM	7.9-15.3	20.7-53.2	N
<u>Controlled Condensation</u>					
H ₂ SO ₄ /SO ₃ (ppm)	Mean	NM	0.81	0.63	2.60
	Range	NM	0.047-1.18	0.34-0.92	2.31-2.69
SO ₂ (ppm)	Mean	NM	1943	262	4217
	Range	NM	1568-2242	256-269	2135-6300
<u>Instrumental Gas Analysis</u>					
SO ₂ (ppm)	Mean	392	1710	226	NM
	Range	383-408	1543-1901	212-242	NM
NO (ppm)	Mean	256	164	79	NM
	Range	246-262	138-191	75-82	NM
NO ₂ (ppm)	Mean	8	8.2	ND	NM
	Range	0-19	4.5-13.4	--	NM
O ₂ (ppm)	Mean	10.8	7.7	13.5	NM
	Range	10.5-11.5	7.2-8.5	13.5-13.5	NM

N = only one sample obtained

NM = no measurements planned

ND = not detectable

*Duct work prior to 8B train scrubber.

TABLE 4-2. SUMMARY OF CONDITIONS AND RESULTS OF MODIFIED
EPA-5 SAMPLING

Unit Number	Date: 9/26/79		10/1/79		10/2/79		10/3/79		10/1/79		10/1/79		10/1/79	
Sampling Time	7	7	7	7	7	7	7	7	8	8	8	8	8	8
Avg. Boiler Load (MW)	1315-1700	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652	1454-1652
Isokinetic	505	422	422	422	422	422	422	422	422	422	422	422	422	422
Stack Temp. °F	140	106	106	106	106	106	106	106	106	106	106	106	106	106
Stack Temp. °C	394.8	263.7	263.7	263.7	263.7	263.7	263.7	263.7	263.7	263.7	263.7	263.7	263.7	263.7
SO ₂	146.0	128.7	128.7	128.7	128.7	128.7	128.7	128.7	128.7	128.7	128.7	128.7	128.7	128.7
H ₂ O	8.82	6.98	6.98	6.98	6.98	6.98	6.98	6.98	6.98	6.98	6.98	6.98	6.98	6.98
Avg. Flow Gas Flow Rate	1,728,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000	1,605,000
ACFM	48,900	45,500	45,500	45,500	45,500	45,500	45,500	45,500	45,500	45,500	45,500	45,500	45,500	45,500
SCCFM	1,086,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000	1,049,000
m ³ /min	36,700	30,800	30,800	30,800	30,800	30,800	30,800	30,800	30,800	30,800	30,800	30,800	30,800	30,800
Total Particulates (g)	2.06	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12	1.12
Particulate Mass Conc.	1.26	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69
g/SCCF	2.89	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56	1.56
Particulate Mass Rate	1.18x10 ⁴	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³	6.33x10 ³
kg/hr	5.36x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³	2.87x10 ³
SO ₂ Conc. (ppm)	1882	1786	1786	1786	1786	1786	1786	1786	1786	1786	1786	1786	1786	1786
SO ₂ Mass Rate (kg/hr)	9.26	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64

*This mass flow only for duct 88; full mass flow into scrubbers is estimated as 11.44.

TABLE 4-3. FLUE GAS CONCENTRATIONS (AND PERCENT OF PARTICULATE LOADING) FOR CERTAIN IONS (IC) AND ELEMENTS (ICP) BY METHOD EPA-5*

Unit (Location)	Total Particulate Loading (g/m ³)	µg/m ³ (Z)							
		F ⁻	Cl ⁻	SO ₂	Na	Ca	Al	Hg	Tl
Unit 7 Stack	2.890	70.2 (0.002)	74.6 (0.003)	10,680 (0.370)	1,615 (0.056)	19,440 (0.672)	46,320 (1.60)	2,641 (0.091)	2,333 (0.081)
Unit 7 Stack	1.579	51.7 (0.003)	<2 (-0)	11,610 (0.735)	539 (0.034)	5,318 (0.337)	24,306 (1.54)	1,451 (0.092)	1,190 (0.075)
Unit 7 Stack	3.200	139 (0.004)	119 (0.004)	11,850 (0.370)	1,510 (0.047)	8,566 (0.268)	54,291 (1.70)	3,478 (0.109)	2,747 (0.086)
Unit 7 Stack	1.516	107 (0.007)	2 (-0)	14,140 (0.933)	2,323 (0.153)	18,320 (1.208)	70,220 (4.63)	4,820 (0.318)	3,744 (0.247)
Unit 8 Stack	0.021	<1 (<0.005)	<2 (<0.01)	5,398 (24.70)	--	732 (3.49)	830 (3.95)	73.2 (0.349)	84.1 (0.400)
Unit 8 Stack	0.009	0.80 (-0)	<2 (-0)	2,358 (26.20)	--	658.8 (7.32)	371.5 (4.13)	43 (0.478)	40.6 (0.451)
Unit 8 Scrubber Inlet	5.609	162 (0.003)	1,596 (0.028)	45,570 (0.812)	6,451 (0.115)	37,005 (0.660)	127,750 (2.28)	5,922 (0.106)	>7,612 (0.136)

*IC = Ion Chromatography

ICP = Inductively Coupled Plasma Emission Spectroscopy

Notes: Concentrations of species have been corrected for filter blank contribution.

All NO₃ values <2 µg/m³

Values in parentheses are in percent of total particulate loading.

"--" indicates that average blank filter concentration was larger than filter weight gain.

TABLE 4-4. SYNOPSIS OF ANDERSEN IMPACTOR RESULTS

Date	Location	Volume Sampled (m ³)	Test Duration (min)	Percent Isokinetic	Mass Concentration (g/m ³)	Mass Percent Less Than 15 μ m	Mass Percent Less Than 2 μ m
9/26/79	Stack 7	0.1199	10	94.8	0.668	77.2	7.9
10/1/79	Stack 7	0.0565	10	91.9	0.347	57.3	15.3
10/2/79	Stack 7	0.0959	15	123.0	0.604	62.6	11.2
10/5/79	Stack 7	0.0856	15	103.8	0.951	48.6	8.2
10/1/79	Stack 8	0.7936	110	85.0	0.00556	49.7	20.7
10/7/79	Stack 8	4.1178	240	87.2	0.0138	79.6	53.2
10/7/79	Duct 88	0.0839	8	104.7	1.60	60.3	10.9

TABLE 4-3. CONTROLLED CONCENTRATION TESTS: CONDITIONS AND DATA

	9/30/79	10/7/79	10/13/79	10/20/79	10/27/79	10/31/79	10/31/79	10/31/79	10/31/79
Stack # (Run)	7 (13)	7 (6)	7 (13)	7 (13)	7 (13)	8 (13)	8 (13)	88 (7)	88 (8)
Sampling Time	10:05-11:06	14:51-14:05	9:45-12:00	13:33-15:30	11:18-13:12	10:37-14:00	9:00-10:24	15:00-16:15	
Avg. Flow Gas Flow Rate									
ACI 9 m ³ /min	1.32e10 ⁰ 4.3e10 ¹	1.44e10 ⁰ 4.1e10 ¹	1.53e10 ⁰ 6.3e10 ¹	1.60e10 ⁰ 4.5e10 ¹	1.41e10 ⁰ 4.6e10 ¹	1.41e10 ⁰ 4.6e10 ¹	0.52e10 ⁰ 1.5e10 ¹	0.45e10 ⁰ 1.3e10 ¹	
DCI 10 m ³ /min	1.08e10 ⁰ 3.0e10 ¹	0.96e10 ⁰ 2.7e10 ¹	1.02e10 ⁰ 2.8e10 ¹	1.06e10 ⁰ 3.0e10 ¹	1.25e10 ⁰ 3.5e10 ¹	1.38e10 ⁰ 3.8e10 ¹	0.37e10 ⁰ 1.0e10 ¹	0.31e10 ⁰ 0.8e10 ¹	
2.0e-10 sec	6.30	6.86	7.76	6.55	8.33	7.28	6.87	7.63	
Flow Gas Temp. °F	235	265	256	258	249	253	258	267	
SO ₂ 75% Min. Control									
ppm	0.47	1.10	0.61	0.97	0.62	0.36	2.69	2.51	
kg/hr net SO ₂	0.067	0.186	0.079	0.097	0.107	0.061	0.090	0.076	
SO ₂ Control									
ppm	1.06	1.07	2.04	2.03	2.69	2.56	0.805	2.15	
kg/hr	11.7	12.7	1.75	1.75	25.3	26.6	16.0	30.7	

TABLE 4-6. INSTRUMENTAL GAS ANALYSIS RESULTS*

		9/30	10/1	10/5	10/7
Stack #		7	7	1-6	8
Sampling Time		1610-1730	1225-1255	1115-1345	1605-1815
SO ₂ (ppm)	Mean	1816	1605	392	226
	Range	1715-1901	1543-1658	383-408	212-242
NO (ppm)	Mean	184	144	256	79
	Range	180-191	138-147	246-262	75-82
NO ₂ (ppm)	Mean	7.5	9	8	0
	Range	4.5-13.4	9-9	0-19	--
O ₂ (%)	Mean	7.2	8.2	10.8	13.5
	Range	7.2-7.3	7.7-8.5	10.5-11.5	13.5-13.5

*Values are as measured, and have not been corrected to a consistent O₂ or CO₂ level.

TABLE 4-7. SUMMARY OF BOILER LOAD, SO₂ LEVELS, AND OPACITY
DATA (FROM TVA'S PLANT LOGS)

Date	9/29/79	9/30/79	10/1/79	10/2/79	10/3/79	10/4/79	10/5/79	10/6/79	10/7/79
Boilers on line	2,3,4,5,6	3,4,5,6,67	3,4,5,6,7,68	3,4,5,6,7,68	3,4,5,6,7	3,4,6,7	3,4,6,7	3,4,5,7,68	2,3,4,7,68
Boiler (No.)	1-6	408	492	484	492	384	384	363	369
Load	7	370	422	-	446	-	446	430	410
Mean	8	-	286	300	-	-	-	170	310
Range	1-6	540-635	272-464	368-512	412-512	381-387	361-790	363-363	251-387
	7	-	305-425	410-440	-	-	420-485	375-485	300-500
	8	-	-	270-305	-	-	-	35-300	300-325
SO ₂ (ppm)	1-6	170	300	360	360	320	380	340	280
Mean	7	-	1900	1750	2100	1900	1800	1800	-
	8*	-	-	300	670	-	-	540	560
Range	1-6	360-380	210-390	340-380	320-380	280-360	370-380	330-360	210-300
	7	-	1700-2100	1500-1900	1500-1800	1600-2000	1600-1900	1700-2000	-
	8*	-	-	150-380	480-750	-	-	150-700	450-780
Opacity (%)	1-6	9	16	13	31	18	14	15	11
Mean	7	14**	57	62	75	82	77	76	76
	8	-	-	17	10	-	-	-	-
Range	1-6	7-13	8-28	6-30	20-40	10-82	10-20	10-20	7-31
	7	7-14**	17-80	51-75	69-83	80-84	71-81	62-80	-
	8	-	-	10-32	9-11	-	-	-	0

*Indicated no data recorded in plant logs

**These data are about twice as high as concurrent EPA-5 data.

**Limit down, opacity reading attributable to ESP.

TABLE 4-8. SUMMARY OF FUEL AND SCRUBBER DATA

Fuel*	Units 1-6	Unit 7	Unit 8
% Ash	9.4-17.4	14.8-15.9	14.5-15.1
% Sulfur	0.7-0.9	2.6	4.1
Scrubber, Unit 8, Train B	Slurry	Filtrate ($\mu\text{g}/\text{ml}$)	Solids (mg/g)
pH	5.6-6.1	--	--
Wt. % Solids	5.27-8.49	--	--
Fluoride	--	<1	--
Chloride	--	212-725	--
Nitrate	--	<34-64	--
Sulfate	--	1635-2009	268-488
Calcium	--	590-776	236-293
Sodium	--	14-22	0.7-1.1
Titanium	--	0.049-0.076	0.585-1.00
Aluminum	--	2.34-3.37	15.4-24.1
Magnesium	--	78-177	6.4-8.3
% Insoluble	--	--	17.3-25.0%

*Fuel data provided by TVA.

TABLE 4-9. SUMMARY OF AIRCRAFT FLIGHTS

Date	Time (EDT)	Flight I.D.	Duration (hrs)	FILTER SAMPLE I.D.		Number of Particle Size ^a Spectra	Comments
				Flight Pattern	NiVol Tandem		
9-26	1415	1	2.1	upwind spiral traverses @5 miles	431 432 001 003	1 2	Unit #8 firing oil; TECO SO ₂ not operating; data not analyzed
9-29	1350	2	2.6	upwind spiral traverses @15 miles	433 434 005 007	1 4	Unit #7 and #8 down; TECO SO ₂ response time inadequate; data not analyzed
9-30	1100	3	0.7	--	--	--	500 VA inverter failure; Unit #8 down; data not analyzed
10-1	1245	3A	2.0	traverses @5 miles	435 009	4	Poor plume definition; data not analyzed
10-1	1526	4	2.6	upwind spiral traverses @3 miles	436 437 011 013	1 4	Poor plume definition; data not analyzed
10-2	1030	5	2.8	upwind spiral traverses @10 miles traverses @20 miles	440 438 015 017 439	2 3 3	All units up
10-2	1700	6	2.5	upwind spiral traverses @10 miles traverses @20 miles	401 402 025 027 403	2 4 2	Unit #8 down
10-3	1049	7	3.0	traverses @6 miles upwind spiral traverses @6 miles	404 405 031 033 406	4 1 3	Unit #8 down; significant change in plume direction and stability
10-3	1536	8	2.5	traverses @16 miles traverses @8 miles	407 408 037 061	2 4	Unit #8 down
10-5	0830	9A	0.7	--	--	--	Fog prevented sampling Unit #8 down
10-5	1200	9	2.5	upwind spiral traverses @3 miles traverses @6 miles	451 410 065 063 409 039	1 4 3	Unit #8 down; Doppler failure-- locations referenced by alternate navigation system
10-6	0933	10	1.5	Center line	-- -- 067 069 -- 071 073	-- -- --	Denuder experiment; Unit #8 firing oil; data not analyzed
10-6	1500	11	2.1	upwind spiral traverses @5 miles traverses @13 miles	452 453 075 077 454 079	1 3 2	Sampling terminated due to rain
10-7	0900	12	2.5	upwind spiral traverses @5 miles traverses @35 miles	455 456 081 083 457 085 27	1 2 3 67	All units up
TOTALS		17	30.7				

^a Represents the number of bag fills processed for particle size data (EAA)

TABLE 4-10. SUMMARY OF MEAN VALUES OF SEVERAL COMPOSITED PLUME
PENETRATION FLIGHTS AND UPWIND SPIRALS

Flight #	Number of Data Points	Downwind Location (miles)	Temp. (°C)	Relative Humidity (%)	CNC (#/cc)	Neph. (10^{-4} m^{-1})	SO ₂ (ppb)	O ₃ (ppb)	NO (ppb)	NO _x (ppb)
5	2366	10	7.27	82.3	38797	1.01	150	42	4.25	5.54
5	2712	20	8.47	76.3	33142	0.94	130	51	8.56	2.66
5	3224	Upwind	7.26	83.1	27365	0.89	80	57	2.21*	1.80
6	2610	10	10.7	75.1	9154	0.93	120	48	1.53	6.76
6	2418	20	12.1	70.6	8621	0.92	120	52	0.23	2.52
6	2398	Upwind	13.4	65.7	8295	0.85	13	60	3.26*	1.03
7	9800	6	11.5	79.8	9563	1.40	129	49	7.42	7.64
7	2892	6	12.6	80.3	16560	1.46	154	46	0.80	5.02
7	2435	Upwind	12.9	81.4	9082	1.46	120	53	4.18*	1.20
8	2804	8	14.9	64.1	14305	1.03	160	57	1.35	4.32
8	2622	16	15.4	60.5	16545	1.02	128	54	4.13	5.41
9	3574	3	6.4	73.0	20521	1.17	190	51	1.87	4.62
9	3276	6	8.1	70.3	19704	1.17	162	54	5.79*	0.94
9	3224	Upwind	6.8	73.0	16905	1.15	160	55	0.11	1.08
11	2458	5	12.5	75.0	15994	0.89	400	72	1.99	6.45
11	1352	13	12.6	75.5	13445	0.87	410	74	0.33	2.50
11	2457	Upwind	13.5	71.9	18734	0.93	320	66	3.80	5.00
12	2682	5	9.8	39.7	53131	0.73	180	43	4.51	9.67
12	2352	35	10.4	44.1	63236	0.58	150	38	5.47*	1.07
12	1819	Upwind	10.2	40.4	26928	1.07	140	38	0.24	0.63
Typical Standard Deviation		0.6	4.0	3000	0.08	40	6	1 to 50**	5 to 70**	

*A few very large values distort NO average.

**Large range in standard deviation observed during different flights. The quality of these data is discussed in the Data Volume.

TABLE 4-11. PLUME AND ATMOSPHERIC BACKGROUND SPECIES CONCENTRATIONS

Flight #	Distance (miles)	Volume Samples (m ³)	Quartz HiVol Filters						Teflon-Nylon Tandem Filters		
			SO ₄ ²⁻ (μg/m ³)	Na (μg/m ³)	Ca (μg/m ³)	Al (μg/m ³)	Mg (μg/m ³)	Ti (μg/m ³)	Volume (m ³)	NO ₃ ⁻ (μg/m ³)	
5	10	0.84	18.0	N	10	N	N	0.47	0.334	N	
5	20	1.05	6.95	N	46	13	22	0.48	0.419	1.7	
5	Upwind	1.34	4.1	60	23	7	8	0.37	0.537	0.9	
6	10	1.09	18.1	N	22	20	6	3.71	0.435	3.2	
6	20	1.01	10.6	N	33	3	11	1.90	0.403	1.5	
6	Upwind	1.00	8.0	N	35	87	5	10.08	0.400	1.8	
7	6	1.28	20.1	N	6	N	3	1.48	0.513	2.7	
7	6	1.08	14.7	56	49	44	13	2.34	0.433	4.8	
7	Upwind	1.02	5.0	N	N	4	N	0.42	0.406	1.7	
9	2-3	1.41	11.7	50	14	7	5	0.91	0.556	1.1	
9	6	1.25	7.9	81	N	N	2	0.74	0.499	1.0	
9	Upwind	0.71	4.4	N	8	13	10	0.70	0.283	3.2	
11	3-6	1.03	7.0	N	N	3	3	2.99	0.410	0.7	
11	13	0.62	11.1	N	6	14	5	3.74	0.225	2.7	
11	Upwind	1.03	9.5	N	18	4	9	0.50	0.410	1.0	
12	5-6	1.11	3.4	N	14	5	8	N	0.445	0.4	
12	35	0.98	4.7	N	12	3	5	0.10	0.392	1.3	
12	Upwind	5.3	N	N	N	N	N	0.05	0.400	0.5	

N - Total weight of filter was less than average blank filter concentrations.

TABLE 4-12. RESULTS OF QUALITY ASSURANCE AUDITS
WIDOWS CREEK, OCTOBER 1979

Monitoring System	Parameter	Mean Relative Error*
Airplane	NO	-9.2
	NO _x	+2.4
	NO ₂	-6.6
	O ₃	+7.7
	SO ₂	+4.3
Stack	NO	-2.1
	NO _x	+0.5
	NO ₂	-6.0
	O ₂	-3.3
	SO ₂	+18.8

*These data are after adjustment, if adjustment was necessary.

SECTION 5

DISCUSSION OF RESULTS

During the two week sampling period, source sampling and airborne measurements were made on seven days. While it may be desirable to perform simultaneous, or preferably time phased sampling at the source and downwind in the plume, it was beyond the scope of this program. Rather, the source was characterized at its nominal operating parameters for subsequent comparison with the downwind plume measurements. The operating parameters of the units were logged during both source characterization and plume measurements to allow proper comparison under similar conditions.

A discussion of results is presented here which describes the source characterization, plume measurements and several specific case studies. The discussion is intended to present the basis for the results, any limitations and conclusions which may be drawn. Finally, the results are compared and contrasted to those of other researchers.

SOURCE CHARACTERIZATION

The source characterization was performed to provide data on the emission rates of primary pollutants from each of the units. As described in Section 3, measurements were conducted for total mass and chemical composition, particle size distribution, gas phase composition, including NO_x , SO_2 and O_2 and the sulfur trioxide/sulfuric acid mist concentration. Additional information was obtained which describes the particle fractional efficiency of the scrubber and the contribution of primary sulfate aerosol by the scrubber. Emphasis was placed on Units 7 and 8, with limited measurements on Units 1 through 6.

Primary Pollutant Emissions

Primary pollutant emissions are summarized in Table 5-1 for Units 1 through 6, 7 and 8. Data are presented for sulfur species (SO_2 , $\text{SO}_3/\text{H}_2\text{SO}_4$ and sulfate), nitrogen oxides (NO , NO_2 , NO_x and nitrate), water and total particulate mass. The data are presented at emission rates to allow evaluation of each Unit's contribution to the total pollutant emissions from the Widows Creek Steam Plant.

TABLE 5-1. MASS EMISSIONS (KG/HR) FROM UNITS 1-6, 7 AND 8
AT THE WIDOWS CREEK STEAM PLANT

Pollutant	Unit 1-6 (~384 MW)	Unit 7 (~430 MW)	Unit 8 (~300 MW)
Total Particulate Mass	--	3800	40
SO ₂	1574	8352	1356
SO ₃ /H ₂ SO ₄ (as SO ₂)	--	5.57	7.34
Sulfate (as SO ₂)	--	14.7	5.3
NO	505	304	212
NO ₂	23.8	30.1	<12
NO _x (as NO)	424	326	212
Nitrate (as NO)	--	<3.37	<2.05
Water	--	94482	119966

-- indicated value not measured.

As may be expected, due to differences in fuel and control devices, emissions vary considerably between the stacks. Only limited data were obtained for Units 1 through 6, so this discussion will emphasize observed differences between Unit 7 and the scrubbed emissions of Unit 8. The scrubbed stack emissions are as expected lower for SO_2 and total particulate mass. Sulfur trioxide ($\text{SO}_3/\text{H}_2\text{SO}_4$ mist) emissions are slightly greater for Unit 8, probably due to the higher sulfur content of the coal feed stock (2.6 vs. 4.2 percent S). The scrubbed unit's sulfate emissions are an order of magnitude greater than would be expected from total mass emissions, when compared to Unit 7. To some extent this may be expected due to differences in coal; however, there is evidence (as discussed in a later section) that the scrubber itself is a significant contributor of sulfate. Nitrogen oxide emissions are significantly greater for Units 1 through 6. This may be the result of the difference in fuel combustion between Units 1 through 6 (wall fired) and Units 7 and 8 (tangentially fired). No primary nitrate emissions were observed over the filter background values. As would be expected, the scrubber did add a greater amount of water, however, the difference was nominally 1.0 percent by volume.

Particle Size Distribution

Particle size distributions for Units 7 and 8 are presented in Figures 5-1 and 5-2 respectively. The data have been plotted as both the cumulative distribution, and the differential distribution expressed as a mass concentration (gm/m^3). The cumulative distribution was log normally transformed and fitted with a natural cubic spline curve fitting method (13) to obtain a smoothed distribution. The histogram (experimental data) and spline fit (smoothed curve) are shown for the differential distributions.

The particle size distribution from Unit 7 appears to be unimodal and approximately log normally distributed. The mass mean diameter is a nominal 8 μm , with a geometric standard deviation of approximately 2.6. In contrast, the Unit 8 particle size distribution is clearly bimodal with modes at nominally 8 and 0.4 μm . Geometric standard deviations of each of the modes are approximately 1.9 and 2.3 respectively. The presence of a fine particle mode in the Unit 8 particulate emissions can be attributed to the particle removal efficiency of the scrubber and will be discussed in more detail in the following section.

It is of interest to characterize the size distributions in terms of inhalable and respirable particle mass fractions. Inhalable particles are defined as less than 15 μm aerodynamic diameter, while respirable particles are defined as less than 2.5 μm aerodynamic diameter. The

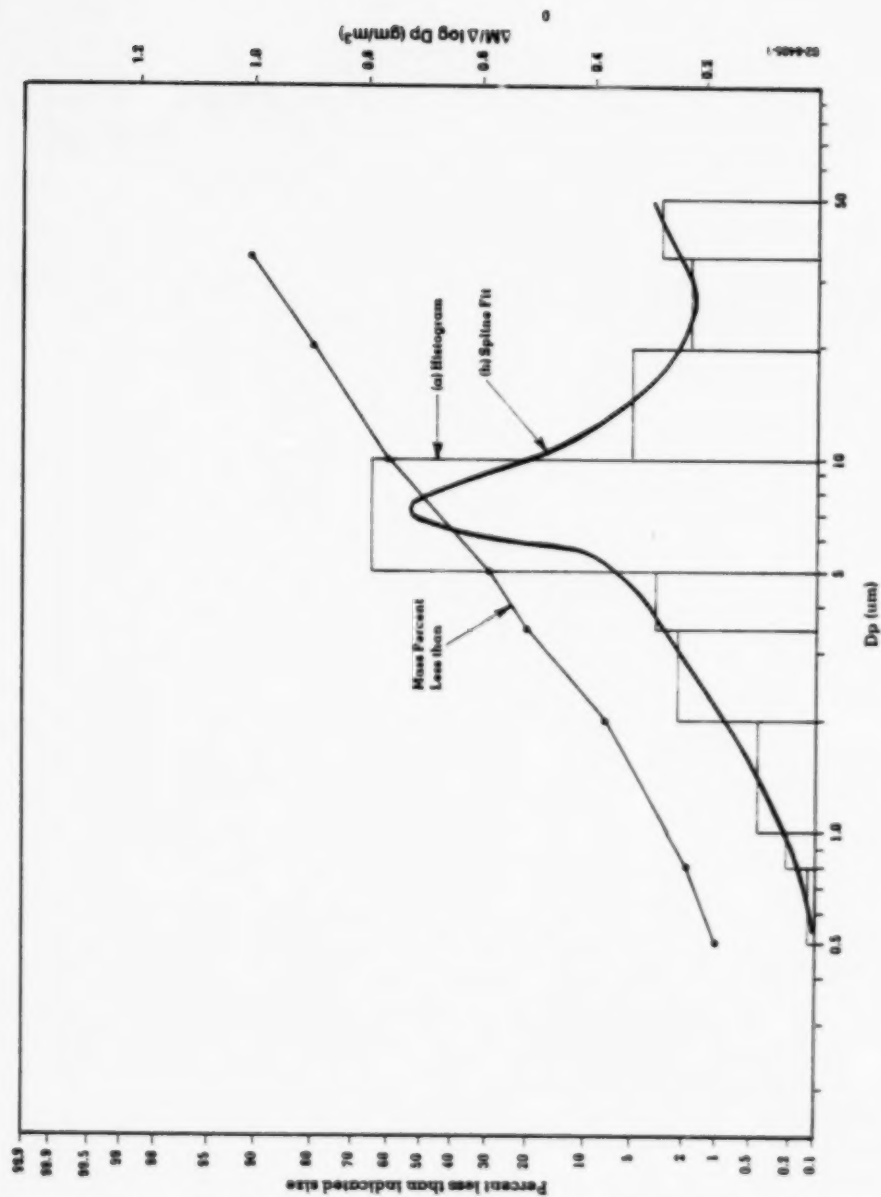


Figure 5-1. Particle Size Distribution for Unit 7.

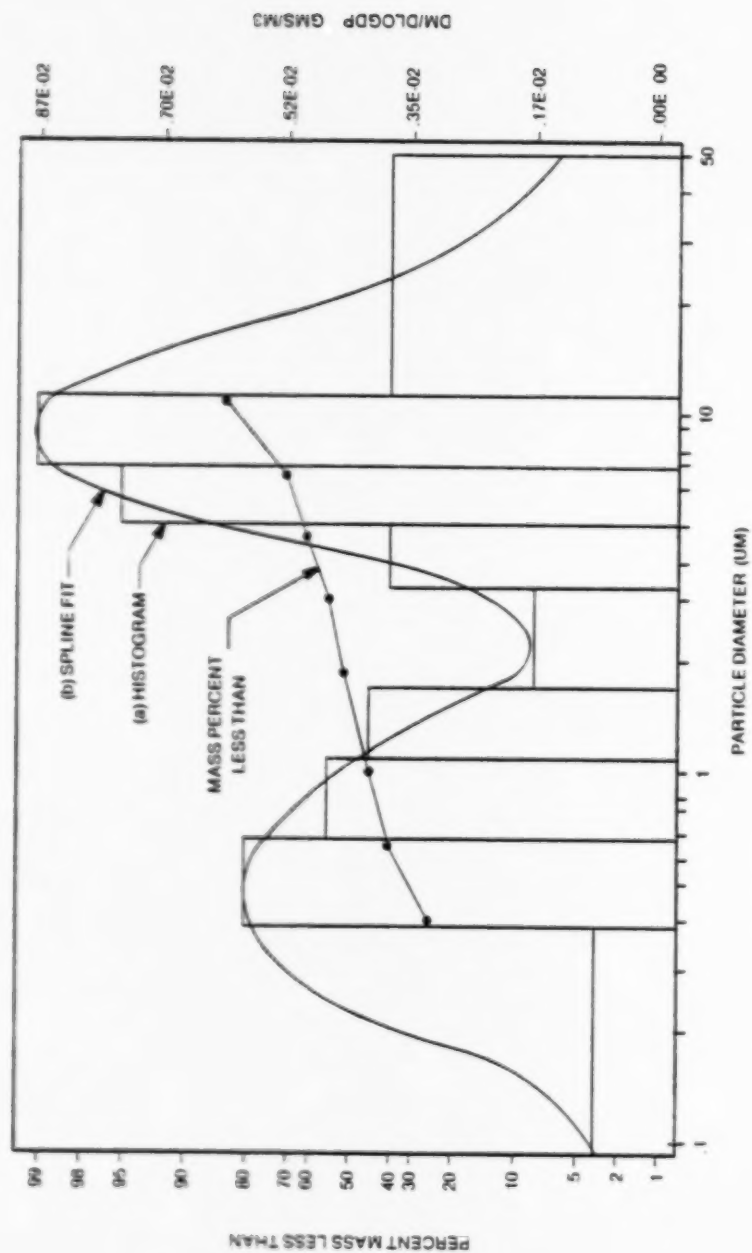


Figure 5-2. Particle Size Distribution for Unit 8

approximate mass fractions were obtained from the Unit 7 and 8 spline fit data. Results are presented in Table 5-2. Of interest is the relatively large respirable mass fraction associated with the scrubbed emissions from Unit 8. However, when put into the perspective of total mass emitted, the respirable mass from Unit 8 is only 2 percent of that of Unit 7.

TABLE 5-2. DISTRIBUTION OF INHALABLE AND RESPIRABLE PARTICLE MASS

Mass Fraction Less Than:	Unit 7 (~430 MW)	Unit 8 (~300 MW)
15 μm (inhalable)	0.70	0.85
2.5 μm (respirable)	0.10	0.50

Scrubber Characterization

Of particular interest during this study was the effect of the scrubbed emissions on downwind transformations. For this reason, the scrubber was characterized both for its particulate removal and contribution of mass, particularly sulfate.

Measurements were made at the inlet of the 8B (Figure 1-1) train scrubber. The volumetric flow through 8B was measured to be approximately 20 percent of the total measured flow from stack 8. For purposes of calculation, it was assumed that removal efficiencies of all scrubber trains performed in a similar manner. Figure 5-3 shows the cumulative and differential particle size distributions for the particulate matter exiting the Unit 8 electrostatic precipitator (ESP) and entering the 8B scrubber train. The particle size distribution is similar to that of Unit 7, showing a single mode at approximately 8 μm diameter, but with a somewhat smaller geometric standard deviation (2.2). The fractional particle penetration through the 8B scrubber train can be defined from the spline fits of the 8B and stack 8 particle size distributions as:

$$P_i = \frac{(DM/D\log D_p)_{\text{Stack 8}}}{(DM/D\log D_p)_{\text{8B}}}$$

where: P_i is the fractional particle penetration for the i th particle size interval and,

$DM/D\log D_p$ is the differential mass concentration for the i th particle size interval of stack 8 and 8B respectively.

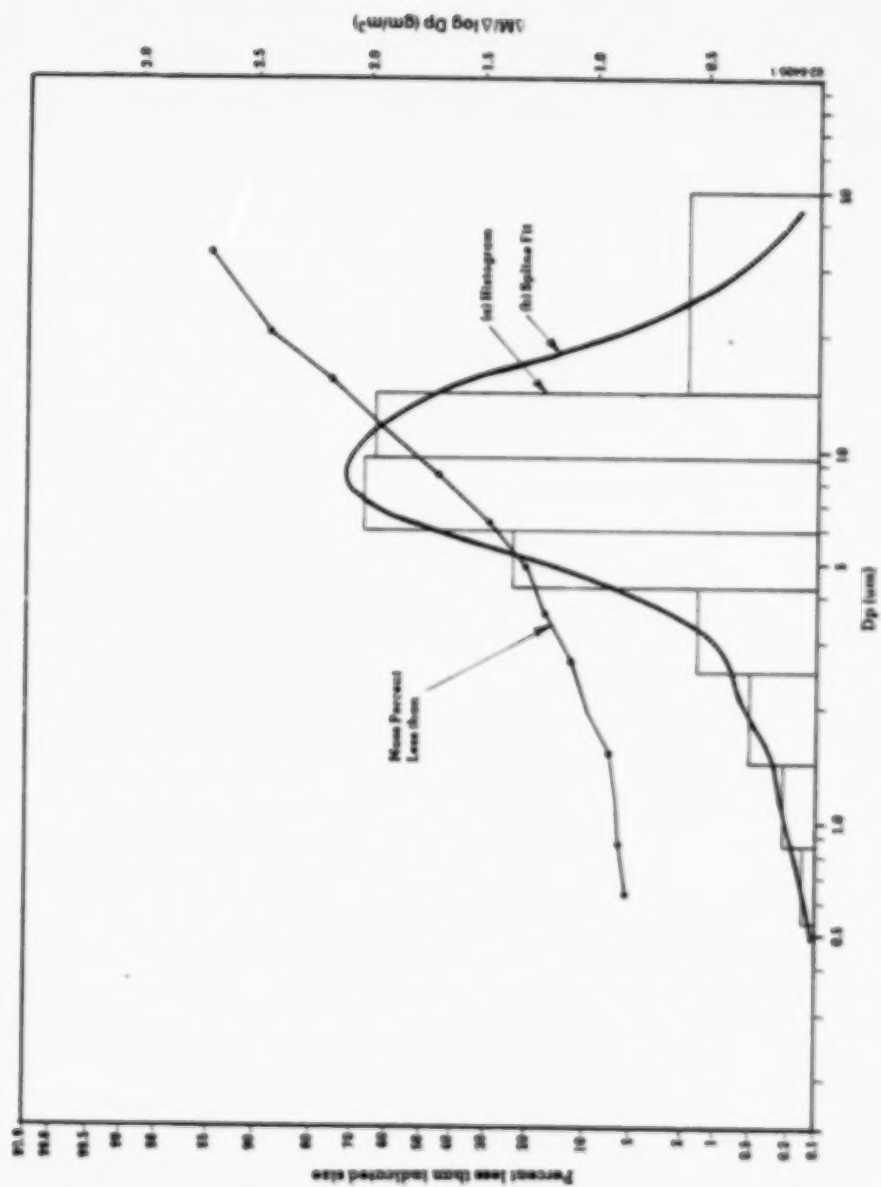


Figure 5-3. Particle Size Distribution for Duct 8B.

If all of the particle size intervals are of equal size, the mass concentration can be substituted for the differential mass concentration. The resulting fractional particle penetration curve is shown in Figure 3-4. The curve shows that the scrubber train is capable of removing particles greater than 2 μm with high efficiency (99.5 percent), however, the removal efficiency falls off rapidly for submicron particles (88 percent). The particle collection characteristics of the scrubber train result in the bimodal particle size distribution observed at stack 8. The overall particulate mass removal efficiency for the scrubber train is approximately 99.8 percent.

The limestone scrubber train was serving as an effective FGD (flue gas desulfurization) system. Based upon simultaneous sampling at the 88 scrubber train inlet and stack 8, greater than 90 percent SO_2 removal was obtained.

As the flue gas passed through the tandem venturi-spray tower scrubber, both SO_2 and particulate matter were removed. The scrubber can, however, contribute mass through entrainment of scrubber liquor high in suspended and/or dissolved solids. The contribution of mass by the scrubber to the total mass penetrating the scrubber can be calculated using the concept of a chemical element balance. If one assumes that the mass flow of species j out of the scrubber, ϕ_j^{out} , is made up of contributions from the fly ash and scrubber liquor entrainment (and subsequent evaporation in the reheater), then the mass balance equation may be written:

$$\phi_j^{\text{out}} = P \phi_j^{\text{in}} + C_j V$$

where:

ϕ_j^{out} = mass flow (g/min) of species j (particles) out of scrubber (into stack)

P = penetration fraction of species j through scrubber

ϕ_j^{in} = mass flow (g/min) of species j into scrubber on fly ash

C_j = concentration of species j in scrubber liquor (g/l)

V = volume rate of scrubber liquor entrained (l/min)

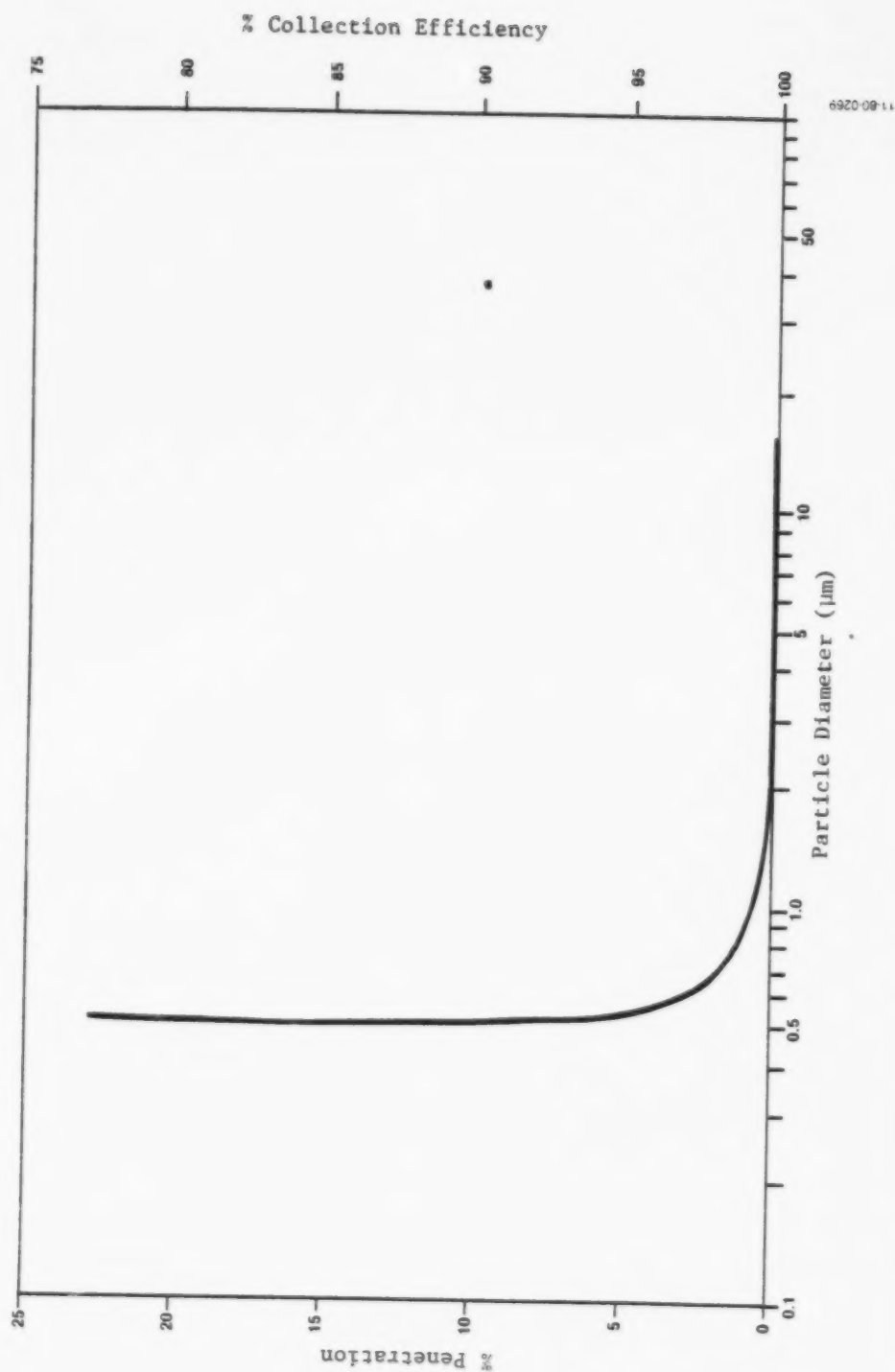


Figure 5-4. Particle Penetration Curve

V should be constant for all species assuming a homogenous (well mixed) scrubber liquor. P will be constant for all species which do not exhibit significant particle size dependence in the incoming flue gas. Previous studies (14,15) suggest such behavior for the cations used in this CEB. ϕ_j^{out} , ϕ_j^{in} and C_j were all measured directly. Particulate composition into and out of the scrubber was obtained from chemical analyses (ion chromatography and ICP) of the EPA Method 5 filter catches (see Table 4-3). Scrubber liquor composition was obtained from similar analyses of scrubber liquor samples (see Table 4-8) collected during the particulate sampling. Results of these analyses as used in the mass balance are presented in Table 5-3.

A multiple variable regression analysis was performed on the set of six equations (one each for Ca, Mg, Al, F⁻, Ti, SO₄²⁻) with three independent (ϕ_j^{out} , ϕ_j^{in} and C_j) and two dependent (V and P) variables. The resultant values that best fit all the data were:

$$V = \text{volume of entrained scrubber liquor} = 34.3 \pm 2.8 \text{ l/min}$$

$$P = \text{fly ash penetration fraction} = 0.00097 \pm 0.00035$$

The error limits represent the standard error of estimate. These results indicate that fly ash penetration through the scrubber is very small, about 0.10 percent. Based upon the above values, the predictions for the mass flows of each specie as well as the total mass can be calculated. Table 5-4 summarizes this information. The predicted mass flow representing primary fly ash penetration is 183 gm/min. If the scrubber liquor mass flow is calculated by difference, the contribution is 131 gm/min. When the contribution is calculated by summing the predicted contribution of the individual species measured, the mass flow is 110 gm/min. Agreement (15 percent) is well within the expected experimental error.

From the above analysis, it can be concluded that of the particulate mass emissions from the scrubbed Unit 8 stack, 40 percent are contributed by the scrubber itself (110-131 gm/min $\div$ 314 gm/min). Furthermore, greater than 90 percent of the sulfate aerosol emissions are generated by the scrubber (59.2 gm/min $\div$ 64.8 gm/min). Further analysis of the data shows that the mass entrained from the scrubber liquor is predominantly dissolved solids and not suspended solids. This is evidenced by the sulfate-aluminum-calcium ratios in the particulate matter, which are similar to the solids dissolved and different from the suspended solids (see Table 4-8). Thus, it can be expected that the scrubber generated mass will contribute to the fine particle size fraction, which is consistent with the observed size distribution.

Finally, the results of the SO₃/H₂SO₄ measurements suggest that the scrubber does not significantly remove SO₃/H₂SO₄ from the flue gas (Table 4-5).

TABLE 5-3. MASS BALANCES ACROSS SO₂ SCRUBBER
(FROM EPA METHOD 5 FILTERS) (g/min)

	Total	Ca ⁺⁺	Mg ⁺⁺	F ⁻¹	Al ⁺⁺⁺	Ti ⁺⁺⁺	SO ₄ ⁻¹
Mass Flow Into Scrubber (g/min), ϕ_j^{in}	188,500	4090	660	19	14,743	1056	5090 ²
Mass Flow Out of Scrubber (g/min), ϕ_j^{out}	314	20.5	1.42	0.056	12.9	1.75	64.8 ²
Scrubber Concentration (g/l), C	--	0.700	0.140	<0.001	0.003	0.0007	1.725

¹ Concentration determined using IC; all others by ICP.

² Filters were maintained at 250°F during sampling, and as such, the sulfate value may include some H₂SO₄.

TABLE 5-4. CALCULATED MASS FLOWS OUT OF SCRUBBER (BEST REGRESSION VALUES)

	Total	Ca ⁺⁺	Mg ⁺⁺	F ⁻	Al ⁺⁺⁺	Ti ⁺⁺⁺	SO ₄ ⁼
Mass from Penetration (gm/min)	183	3.97	0.64	0.018	14.30	1.02	4.94
Mass from Entrainment (gm/min)	>86.6*	23.98	3.36	0.34	0.10	0.024	59.10

*This is the sum of the species measured.

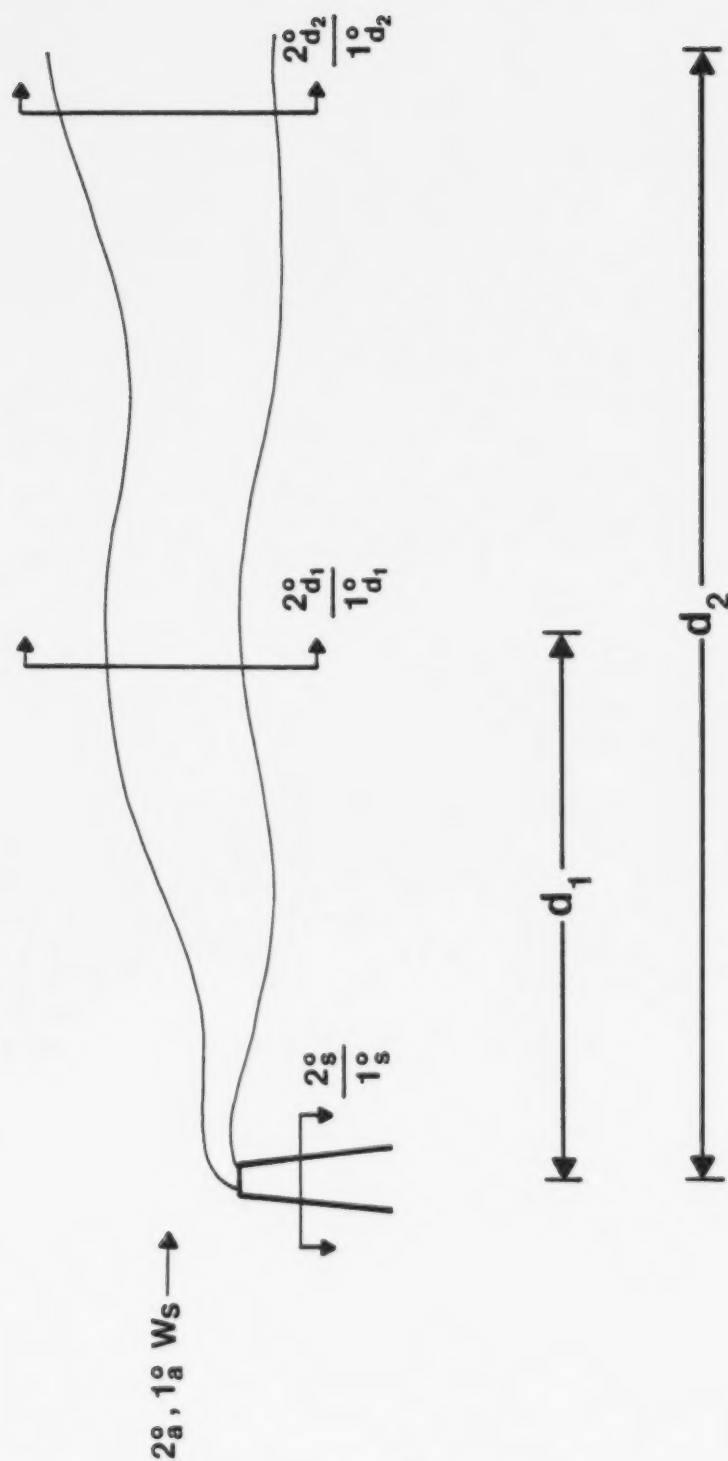
PLUME CHARACTERIZATION

Plume characterization was based upon results of plume cross-sectional analyses downwind of the Widows Creek Steam Plant. The downwind distance was related to a plume travel time or plume age based upon wind speed information obtained from pilot balloon (pibal) releases during the flights. Data collected during upwind spirals were used to correct for the ambient background level of the pollutants measured. Data from six of the most representative flights were analyzed (see Table 4-9). This discussion will focus upon the development of sulfate and nitrate transformation rate information from the measurements made.

Development of a transformation rate was approached from the following concepts (Figure 5-5). Pollutants were assumed to be emitted from a source at a constant rate such that a relationship could be obtained between the secondary pollutant (2_s°) of concern (SO_4° or NO_3°) and a primary pollutant (1_s°). It was assumed that this primary pollutant (1_d°) would show no net gain or loss as it dispersed downwind. Its concentration would exhibit only the effect of dilution. Thus the measured concentrations of the primary pollutant could be used to normalize the measured concentration of the secondary pollutant for the effect of dilution, at the various downwind distances. The measured concentrations of primary and secondary pollutants could presumably be corrected for the background concentration levels of the diluting ambient air (2_a° , 1_a°), based upon upwind ambient measurements. The result of this treatment would allow any net gain of secondary pollutant to be evaluated. Furthermore, it was assumed that the distances at which the downwind pollutant measurements were made could be related to the reaction time by the measured wind speed (W_s). Thus a transformation rate could be calculated based upon (1) the observed net gain of secondary pollutant and (2) the time over which the reaction occurred.

Analysis of the Widows Creek sulfate data was performed using sulfur as the primary pollutant to determine downwind dilution. Sulfur included both SO_2 and SO_4° (as SO_2) in order to account for any net loss of SO_2 to SO_4° .

Results are presented in Table 5-5 for the calculation of sulfate transformation rates. In reality, the SO_4° term in the denominator represents less than five percent of the SO_2 term and as such is within typical confidence limits of the SO_2 measurement. For this reason, SO_2 can be and is often used alone, without correcting for any loss to SO_4° . The values for SO_2 used in the calculation were obtained by averaging the measured SO_2 data (1 observation per 0.5 seconds) over the periods of the hivol filter sampling for SO_4° (for example see Table 5-8). The measured sulfate concentration was expressed as an equivalent volume of SO_2 for purposes of the calculations. Both SO_2 and SO_4° have been corrected for their respective background ambient levels based upon measured upwind values. The sulfate measured in the plume has not been corrected for any source contributions (see case study - flight 5). The plume age was calculated based upon the downwind distance of the



11-80-0361-1

Figure 5-5. Approach for Measuring Pollutant Transformation Rate

TABLE 5-5. CALCULATED SULFATE TRANSFORMATION RATES
DURING THE WIDOWS CREEK PLUME STUDY

Flight #	$\frac{SO_4^{=}}{SO_4^{=} + SO_2} \times 100^*$	Plume Age (hrs)	Percent-hr ⁻¹
5	4.75	1.1	4.3
	1.27	2.2	0.6
6	14.6	0.6	24.3
	2.19	1.2	1.8
7	16.4	0.5	32.7
	8.84	0.6	14.7
9	5.59	0.2	28.
	45.	0.5	90.
11	--	0.2	<0.3
	0.47	0.5	0.9
12	--	0.4	<0.3
	--	3.5	<0.3

*Corrected for upwind ambient background levels of SO₂ and SO₄⁼.

--Indicates measured values were at or below upwind ambient background levels of SO₂ and/or SO₄⁼.

traverse (recorded from the aircrafts RNAV system) and the calculated wind speed (from pibal releases) at the nominal plume centerline.

In general, the results obtained are indicative of the daily plume behavior observed during the study. During all flights the prevailing wind direction was from the west, ranging from west southwest to northwest. This wind tended to disperse the plume into the Tennessee River Valley and/or impact it on the Sand Mountain Range, about one mile from the plant. Observations by the source sampling team routinely recorded that the plumes quickly mixed and impacted on Sand Mountain. From the air, the Widows Creek Steam Plant plume could be observed to fumigate the Tennessee River Valley and channel through the numerous hills and valleys. The river valley was also observed to trap pollutants from other sources, including a nearby paper pulp mill. Plume definition was typically poor with upwind ambient background levels of CNC, b_{sp} and SO_2 often at or above downwind plume values. The Widows Creek site was in fact chosen by Hanna (16) to study plume irregularities caused by the effects of complex terrain. Based upon these observations, it could be expected that high SO_2 deposition velocities would occur near the steam plant. Sehmel has reported that SO_2 deposition velocities can be one to two orders of magnitude greater than particle deposition (17). Gillani, et al. have also reported significant dry SO_2 removal (27 percent) over vegetated land (18). If this was the case, calculated transformation rates would be high, based upon this treatment of the data. Indeed, most values are an order of magnitude greater than the typical 1-10 percent-hr⁻¹ values calculated during other studies (5). Additionally, no significant increases in particle concentration (CNC, b_{sp}) were observed, to support these high transformation rates.

It had been hoped that several trace elements could be used to calculate downwind dilution, in a manner similar to that of sulfur. However, the levels of trace elements measured in the plume were not significantly above background levels of the filters and/or ambient concentrations.

Similarly, the levels of NO_3^- did not occur at values significantly above the background levels of the filters and/or ambient background. For this reason, NO_3^- transformation rates could not be calculated. Based upon the limitations of sampling time, and specie limit of detection above the ambient background, the minimum detectable NO_3^- transformation rate is 12 percent-hr⁻¹. Similar calculations for SO_4^{2-} give a minimum detectable transformation rate of 0.3 percent-hr⁻¹. Previous researchers have used the ratio of SO_2/NO_x as a gross indicator of relative reactivity (4,5). Data from this study suggests that NO_x is reacting at a higher rate than SO_2 , since the SO_2/NO_x ratio increases with plume age. It would be reasonable from this discussion to assume that the NO_3^- transformation rate is between 0.5 percent-hr⁻¹ and 12 percent-hr⁻¹. More than qualitative information from this treatment of the data is not recommended, due to the confidence limits of the SO_2 and NO_x data.

Further analysis of the data is limited to a case study of Flight 5 and the general discussion of Flight 7 which follows. Flight 7 was composed of two penetration sequences at the same distance from the stacks (plume age) about 90 minutes apart. Wind direction, speed and plant load were nearly the same during the two sampling sequences. The SO_2 measurements varied 18 percent; NO_x , 26 percent; CNC, 54 percent; and SO_4^{2-} , 17 percent. Calculated sulfate transformation rates differ by a factor of two. Two identical EAA upwind measurements showed differences of about 15 percent in the Aitken range and about 7 percent in the accumulation size range. These values may represent measures of actual fluctuations, sampling variability, or instrument or flight reproducibility. They are not to be construed as error limits, but they do give some idea of the reproducibility of the data.

Case Study--Flight 5

Flight 5 was chosen to present as a case study since the plume definition was superior to most flights. This is probably attributable to the fact that the flight was flown during the morning hours, prior to the development of vertical mixing. The presence of fog and/or rain during this study typically allowed only late morning, or more commonly, afternoon flights.

A cold front passed through the Widows Creek area during the predawn hours, bringing light thunderstorms to the area. By sunrise, the cloudy skies broke, leaving partly cloudy conditions. Pilot balloon data are shown in Table 5-6. Winds were westerly to west-northwest. Wind speeds ranged from four to seven m/s. A temperature profile performed at 12:18 showed a near adiabatic lapse rate.

Prior to and during Flight 5 all units were operational, with Units 1-6 at 500 MW, Unit 7 at 445 MW and Unit 8 at 300 MW. Flight 5 was performed between 9:45 and 11:45 CDT. The positions of the upwind spiral and two downwind traverses performed during Flight 5 are shown in Figure 5-6. The upwind spiral was performed over Stevenson between 600 m and 1300 m. Nine plume penetrations were executed at gradually decreasing altitudes (1000 m to 800 m) 16 km downwind of the plant. Five more plume penetrations were executed at gradually decreasing altitudes (1000 m - 700 m) 32 km from the plant.

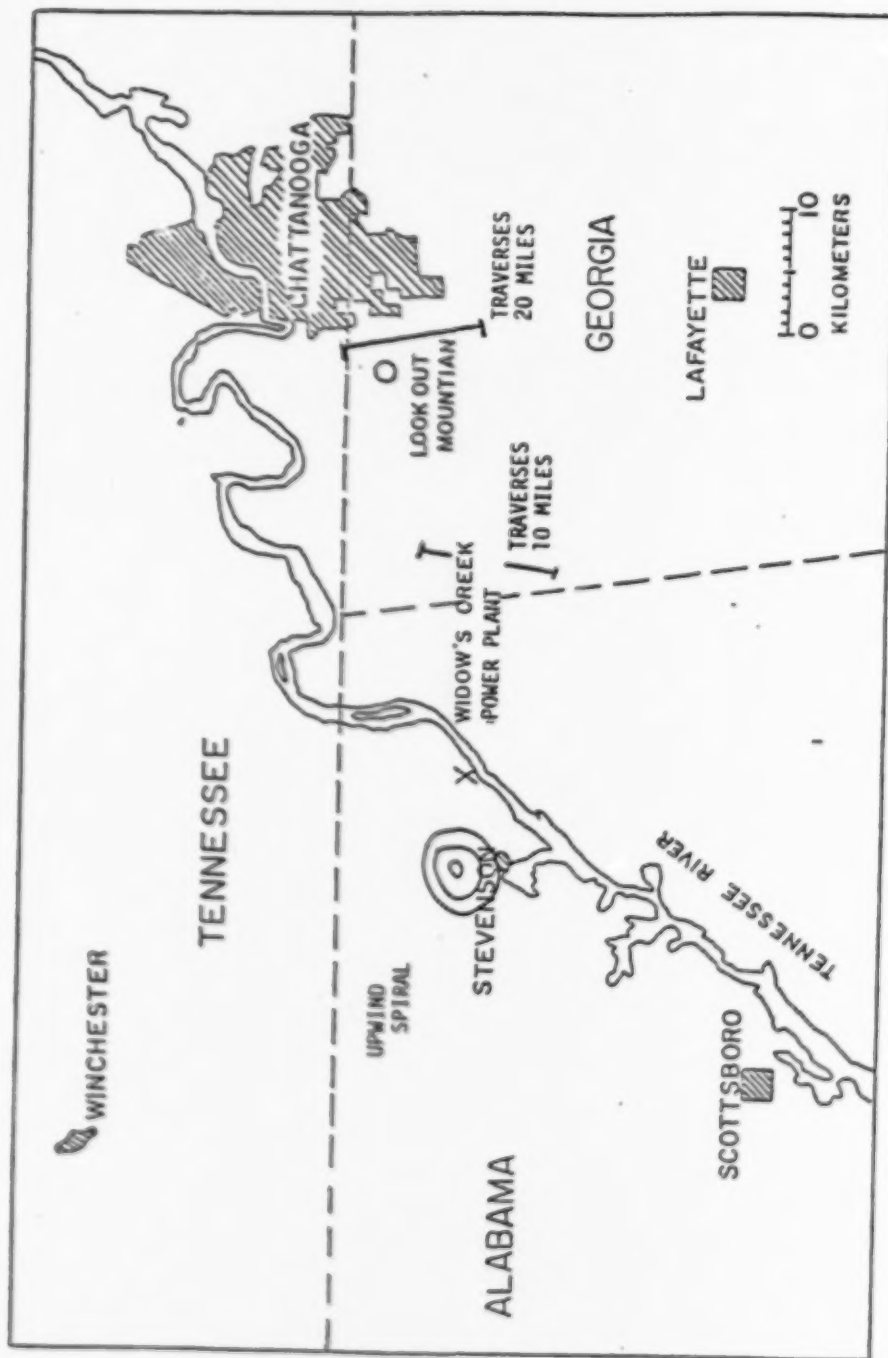
Table 5-7 summarizes the measured ambient background levels. Computer generated plots of concentration versus altitude show slight variations for ozone and CNC with altitude. The measured sulfate concentration (corrected for blank) was $4.1 \mu\text{g}/\text{m}^3$.

As shown by the data in Figure 5-7, the plume was well defined at 16 km downwind. Similar definition was observed at 32 km (Figure 5-8). Ozone showed consistent depletion in the plume, correlating well with the NO_x data. Contour plots at 16 km downwind for selected pollutants were generated based upon computer plots, as shown in Figure 5-9, for CNC. Plots for SO_2 (Figure 5-10) and NO_x (Figure 5-11) suggest that two separate plume centerlines have

TABLE 5-6 . METEOROLOGICAL DATA DURING FLIGHT #5

Altitude Above MSL*	Temperature at 1218 °C	Wind at 1030		Wind at 1100		Wind at 1220	
		Speed M/S	Dir °	Speed M/S	Dir °	Speed M/S	Dir °
242	19.1	3.5	271	2.4	297	4.1	293
332	18.4	4.7	272	2.6	290	2.9	279
423	17.5	4.9	275	2.5	291	4.2	294
513	16.8	4.2	274	2.0	288	3.5	283
603	15.7	3.4	289	3.3	280	4.2	281
692	14.8	3.9	290	4.5	258	5.0	272
781	13.7	4.3	291	5.3	250	3.3	265
869	13.0	6.1	281	7.2	249	2.8	258
957	12.3	5.8	287	7.0	266	4.8	260

*Altitude at ground level, 195 ft (SL).



FLIGHT 5

Figure 5-6. Mapped flight plan for Flight 5.

TABLE 5-7. SUMMARY OF PARAMETERS MEASURED DURING UPWIND SPIRAL

FLIGHT 5

Variable Parameter	Number of Measurements	Mean	Standard Deviation	Coefficient of Variation*	Minimum Value	Maximum Value
Temperature (°C)	3224	7.26	1.7	23.4	3.95	11.05
Dew Point (°C)	3224	4.49	1.0	22.3	-0.14	6.30
Relative Humidity (%)	3224	83.1	8.4	10.1	65.2	106.9
CNC (#/cc)	3224	27365.	3479	12.7	12000.	37900.
Nephelometer (10^{-8} m^{-1})	3224	0.89	0.09	10.1	0.52	1.50
SO ₂ (ppm)	3224	0.08	0.03	37.5	0.02	0.15
O ₃ (ppb)	3224	57.05	3.75	6.6	39.89	73.30
NO (ppb)	3224	2.21	15.0	678.7	0.0	199.80
NO ₂ (ppb)	3224	0.92	10.1	1097.8	0.0	123.40
NO _x (ppb)	3224	1.80	16.2	900.0	0.0	167.40
SO ₄ ²⁻ (ppb as SO ₂)	1	1.07	--	--	--	--

*Coefficient of variation = standard deviation divided by $\sqrt{N}$.

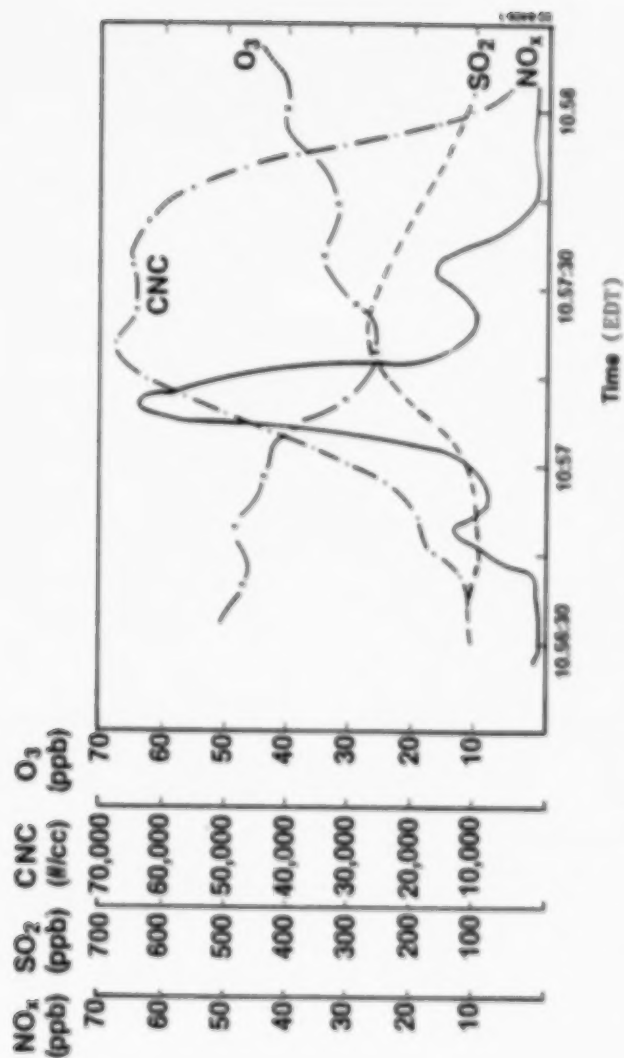


Figure 5-7. Pollutant Profiles at 16 km Downwind during Flight 5, Penetration #2.

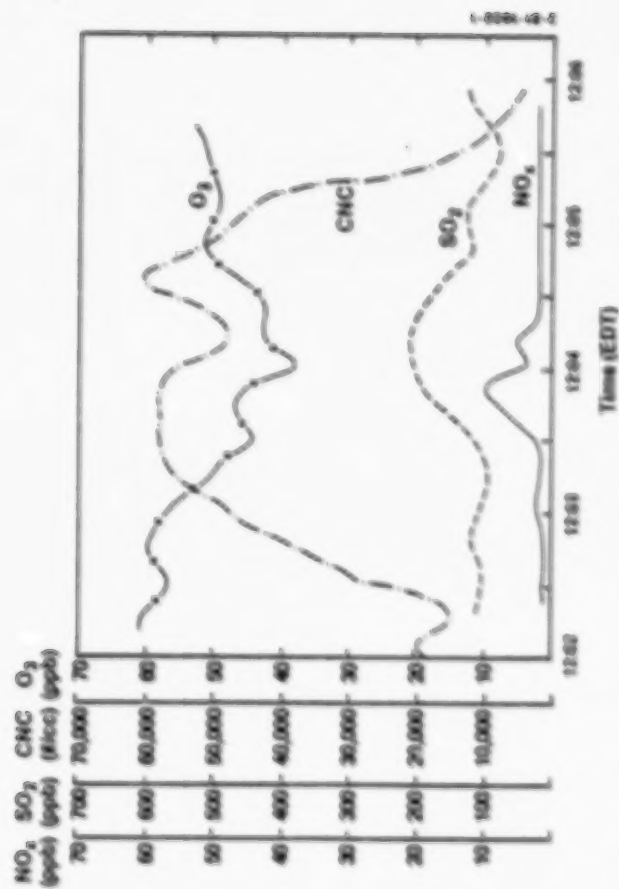
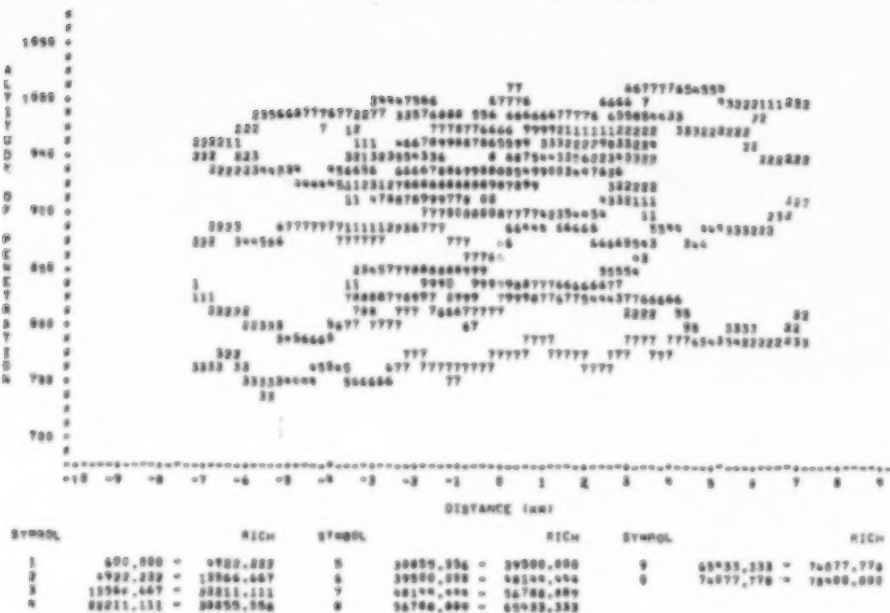


Figure 5-8. Pollutant Profiles at 32 Km Downwind during Flight 5, Penetration #14.

A. COMPUTER PRINT-OUT OF MEASURED VALUES



8. ESTIMATED CONCENTRATION ISOPLETHS

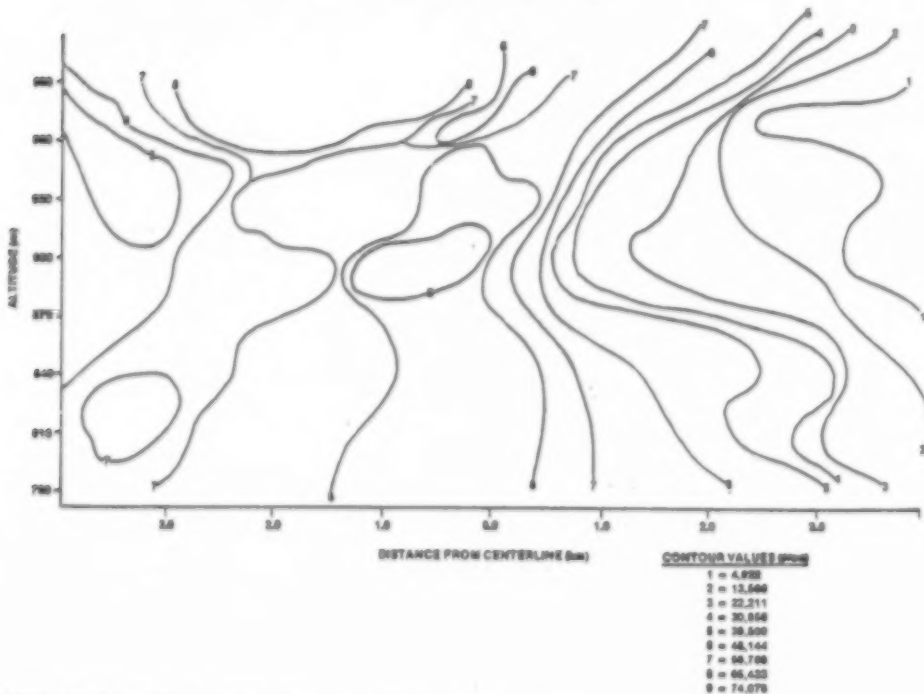
^aCenter of plume was defined by ClC and SO₂ penetration contours.

Figure 5-10.
CONTOUR PLOTS FOR FLIGHT #5, 16 KM DOWNWIND
SO₂

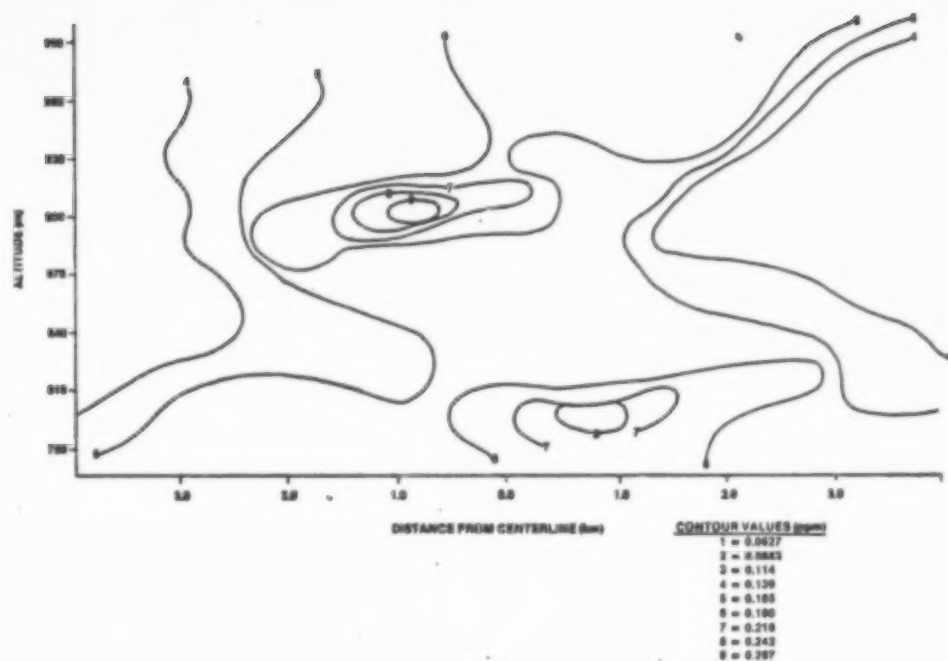
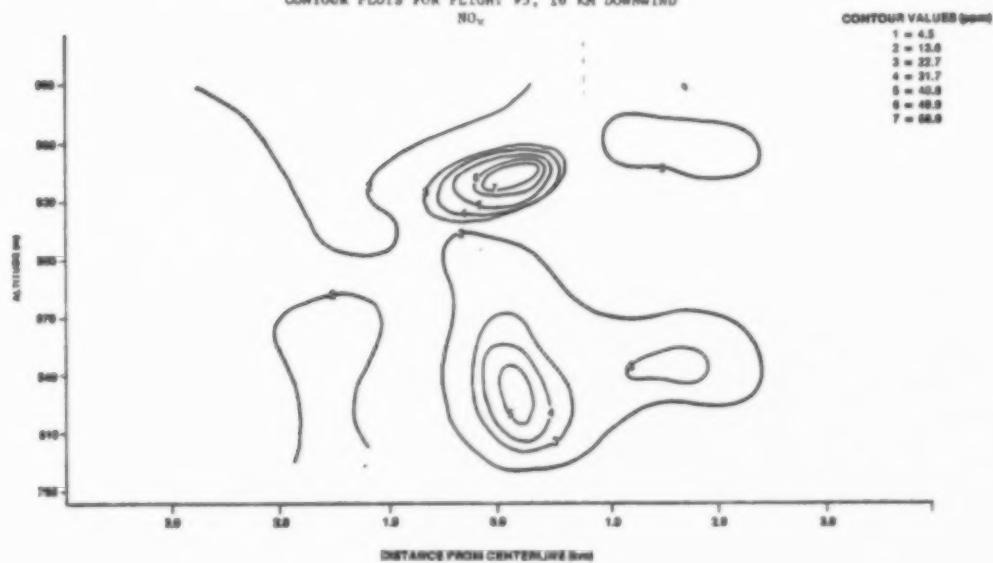


Figure 5-11.
CONTOUR PLOTS FOR FLIGHT #5, 16 KM DOWNWIND
NO_x



been resolved. Based upon the measured NO_x/SO_2 ratio, the upper plume would be identified as Unit 1-6, while the lower plume would be the mixture of Units 7 and 8. The nominal centerlines are separated by approximately 100 meters. Similar definition is seen at 32 km downwind from the contours for SO_2 (Figure 5-12) and O_3 (Figure 5-13). Pollutant concentrations were averaged over the filter collection periods for both 16 km and 32 km traverses. The values along with the measured SO_4^{2-} concentrations are summarized in Table 5-8.

The calculated transformation rates for SO_4^{2-} were 4.3 percent-hr⁻¹ and 0.6 percent-hr⁻¹ at 16 km and 32 km, respectively. These values were calculated as previously described. At 32 km the measured $\text{SO}_4^{2-}/\text{SO}_2 + \text{SO}_4^{2-}$ ratio showed a net loss of SO_4^{2-} from what would be predicted by the $\text{SO}_4^{2-}/\text{SO}_2 + \text{SO}_4^{2-}$ ratio at 16 km. Several explanations for this observation may be offered. Most obvious would be either a net gain of SO_2 or net loss of SO_4^{2-} . Ambient levels of SO_2 at long distances downwind in the plume were not significantly greater than levels measured upwind. This suggests that there was no obvious input of SO_2 to the plume. An apparent net loss of SO_4^{2-} could occur if collection was not significantly above background levels, as would be the case if the plume was very dilute.

Both of these transformation rates have been calculated assuming no SO_4^{2-} contribution from the source. Based upon the SO_4^{2-} and SO_2 emission data measured during this study, a $\text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-})$ ratio for the source can be estimated. Assuming a sulfate emission rate for Units 1-6 based upon Unit 7 data and the sulfur content of their respective coal, a value of 0.21 percent was obtained. This value can be used to correct the previously defined transformation rates to 4.1 percent-hr⁻¹ and 0.5 percent-hr⁻¹ for 16 km and 32 km downwind, respectively. Based upon the above treatment of the data, primary sulfate accounted for between 4 and 17 percent of the total sulfate measured downwind in the plume.

Particle size distribution data were obtained by an Electrical Aerosol Analyzer (EAA) on bag samples during both upwind spirals and downwind plume traverses at 16 km (Figure 5-14) and 32 km (Figure 5-15). The EAA data from Flight 5 along with coinciding CNC data are presented in Table 5-9. Particle size data can be used as an indicator of secondary aerosol formation mechanisms. Recent information suggests that secondary aerosol formation will occur homogeneously (new particle formation) when available surface area is below 500 $\mu\text{m}^2/\text{cm}^3$ (19,20). Available surface area (as calculated from EAA data) in the plume during Flight 5 was nominally 200 $\mu\text{m}^2/\text{cm}^3$. Further support of a homogeneous mechanism comes from a comparison of particle number/volume ratios. In plume values are an order of magnitude greater than background or out of plume values. There is no evidence of a change in the plume of the volume concentration from that in the background, whereas the number concentration increases significantly in the plume. Similar results were obtained during other flights, with the exception being when penetrations were made very close to the source. During such flights (Flight 9), the volume concentration was observed to increase significantly, while the number concentration increased only slightly.

Figure 5-12.
CONTOUR PLOT FOR FLIGHT #3, 32 KM DOWNWIND
ASSUMING TWO MINUTE PLUME WIDTH
SO₂

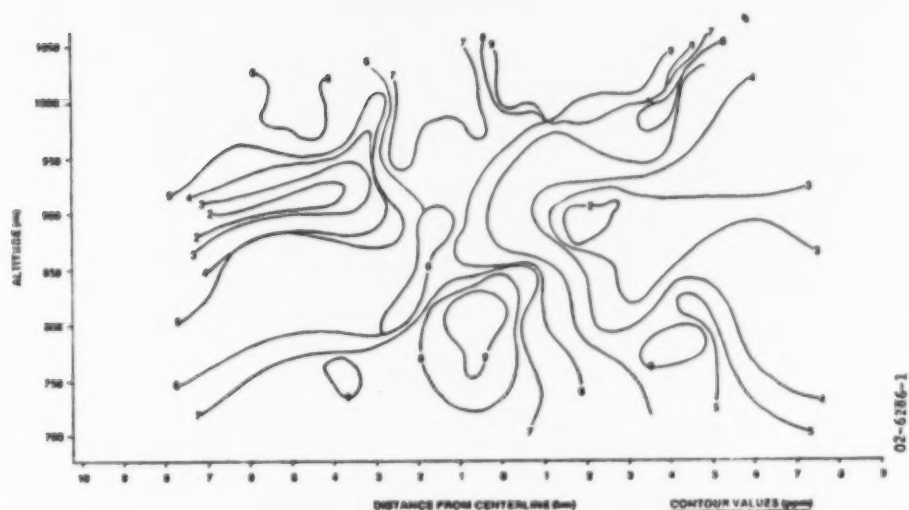


Figure 5-13.
CONTOUR PLOT FOR FLIGHT #3, 32 KM DOWNWIND
ASSUMING TWO MINUTE PLUME WIDTH
O₃

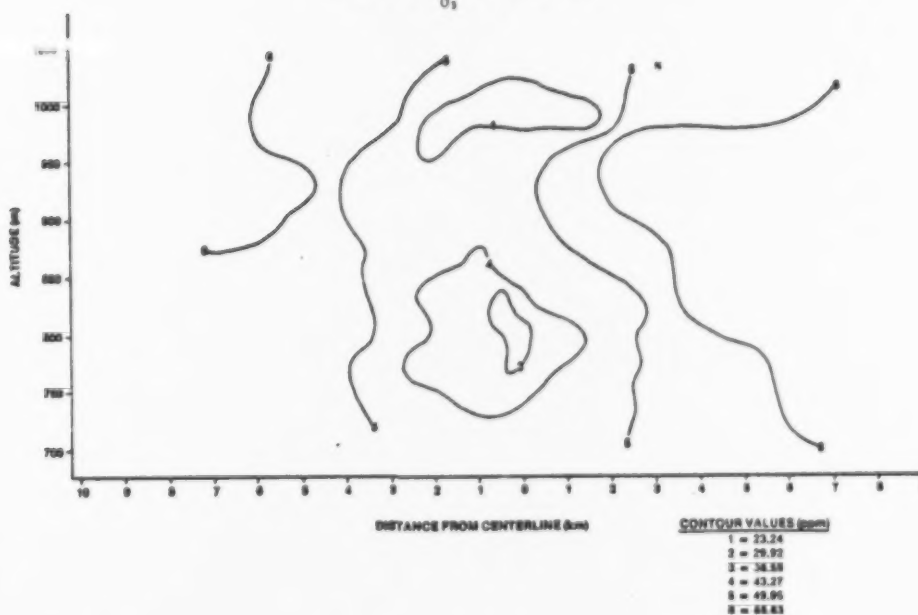


TABLE 5-8. SUMMARY OF FLIGHT 5 DATA BY FILTER TIMES

Distance Downwind	Parameter	N	Mean	Standard Deviation	C.V.	Minimum Value	Maximum Value
16 km	Temperature (°C)	2366	7.27	0.55	7.6	6.33	8.48
	Relative Humidity (%)	2366	82.31	13.7	16.6	44.67	119.15
	CNC	2366	38797.	23323.	60.1	913.	78040.
	Nephelometer (10^{-4} m^{-1})	2366	1.01	0.12	11.9	0.77	1.45
	Ozone (ppb)	2366	42.07	6.6	15.7	23.20	57.01
	SO ₂ (ppm)	2366	0.15	0.04	26.7	0.06	0.27
	NO (ppb)	2366	4.25	17.5	412.	0	176.95
	NO _x (ppb)	2366	5.54	8.8	159.	0	64.21
	SO _x (ppb as SO ₂)	1	4.68	--	--	--	--
32 km	Temperature (°C)	2712	8.47	0.96	11.3	6.84	10.16
	Relative Humidity (%)	2712	76.28	10.2	13.4	47.47	99.22
	CNC (#/cc)	2712	33142.	17283.	52.1	4940.	56167.
	Nephelometer (10^{-4} m^{-1})	2712	0.94	9.07	7.4	0.71	1.16
	Ozone (ppb)	2712	50.59	5.2	10.3	36.19	61.92
	SO ₂ (ppm)	2712	0.13	.04	30.8	0.031	0.21
	NO (ppb)	2712	8.56	39.3	459.	0	442.87
	NO _x (ppb)	2712	2.66	11.4	428.	0	167.08
	SO _x (ppb as SO ₂)	1	1.69	--	--	--	--

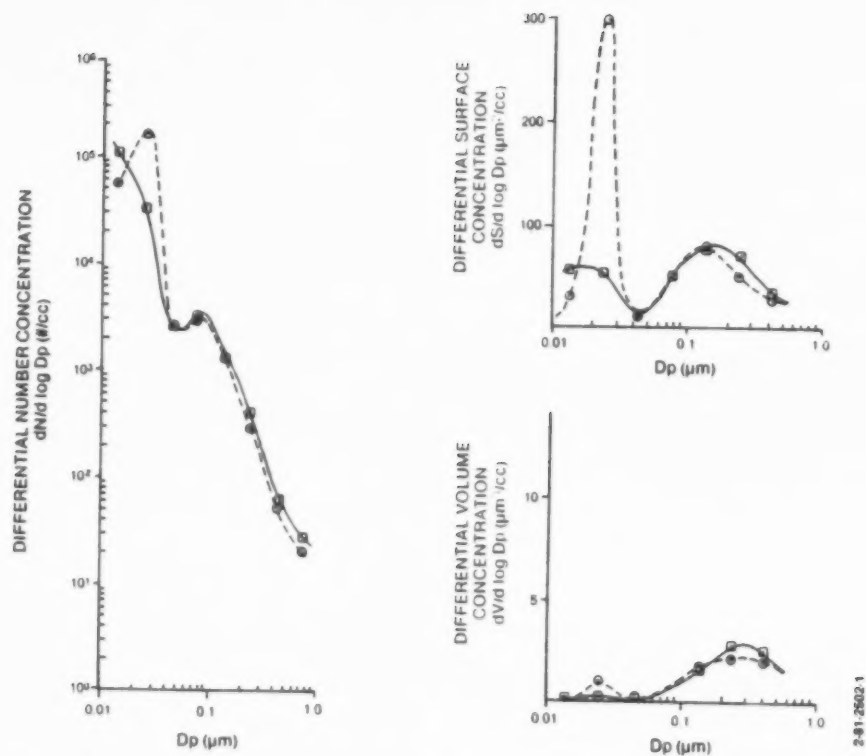


Figure 5-14. Differential number ($dN/d \log D_p$), surface ($dS/d \log D_p$) and volume ($dV/d \log D_p$) distributions measured during Flight 5 at 16 km downwind. The upwind ambient distribution is also shown (dotted line).

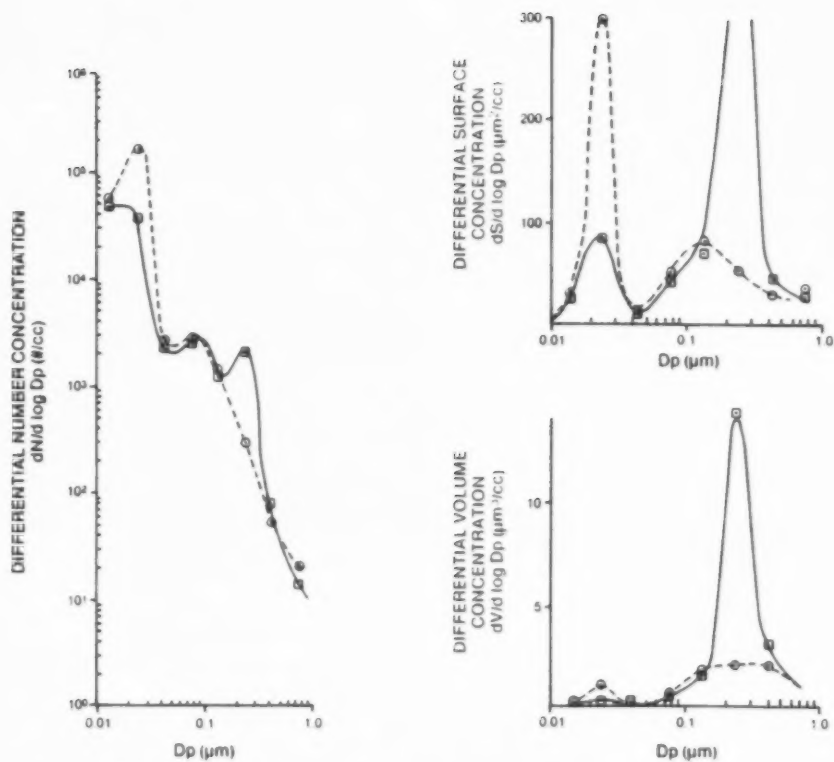


Figure 5-15. Differential number ($dN/d \log D_p$), surface ($dS/d \log D_p$) and volume ($dV/d \log D_p$) distributions measured during Flight 5 at 32 km downwind. The upwind ambient distribution is also shown (dotted line).

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TABLE 5-9. PARTICLE DATA FROM FLIGHT 5

Flight #	Bag #	Distance (km)	Location	Accumulation Volume ($\mu\text{m}^3/\text{cc}$)	CNC (#/cc)
5	1	16	plume edge	6.87	2,500
5	2	16	plume edge	4.17	3,300
5	3	16	in plume	3.56	79,000
5	4	32	in plume	2.72	47,000
5	5	32	in plume	3.29	48,000
5	6	32	in plume	3.16	51,000
5	7	upwind	---	4.29	27,400

COMPARISON WITH OTHER STUDIES

The topic of gas-to-particle conversion processes has been one of growing interest in the past several years. A central concern is the formation of sulfate particles, which are thought to be prominently involved in the acid rain and visibility problems. Available information also indicates that nitrates play a significant role. Power plants are suspected to be major contributors, both as primary emitters of sulfates and as emitters of SO_x and NO_x , likely precursors of sulfates and nitrates. One of the original objectives of this project was to determine the effect an SO_2 scrubber would have on primary and secondary sulfate formation. Due to unit availability and meteorological problems, the specific effects of the scrubbed plume could not be elucidated.

It is useful to compare the results of this study to other recent work. Hegg and Hobbs (5) have recently surveyed much of the gas-to-particle literature for power plant plumes. As they point out, several different techniques have been used to measure and calculate the gas-to-particle conversion rates, and comparison of results may reflect differences in technique as much as real differences. For example, Hegg and Hobbs (5) report the results of 14 different studies for rates of SO_2 oxidation in power plant plumes; half of the studies are since 1977. At least five different methods were used to determine the SO_2 oxidation rate; lately, most authors, including the authors of this report, have used the ratio of the particulate sulfate to total sulfur. Reported values for percent per hour SO_2 oxidation range from 0 to 300 percent-hr⁻¹, but most recent studies are between 0 and 10 percent-hr⁻¹. The case selected for intensive study in this work determined the rates to range from 0.6 to 4.5 percent-hr⁻¹.

The surface area of the plume particles was not large e.g., Flight 5 at 16 km (67 minutes), $A = 166 \mu\text{m}^2/\text{cm}^3$; Flight 9 at 4 km (15 minutes), $A = 435 \mu\text{m}^2/\text{cm}^3$. Based on work by Whitby (19) and Friedlander (20), condensation in the accumulation mode is dominant only above about $500 \mu\text{m}^2/\text{cm}^3$. The number of Aitken particle does not appear to be large in this study (e.g., see Table 5-13 and Data Volume), but the high background level of Aitken particles may obscure the results.

Several authors have also reported results involving the particle volume formation rate (21). If it is assumed that most of this volume formation activity occurs below one micron (even though the total volume is dominated by particles greater than one micron), then the volume of Aitken plume accumulation mode particles in Table 5-13 may approximate the particle formation volume. Again, high background levels cast doubt on the validity of the calculation of such a value for Flight 5, but the ratio of the particle volume formation rate to the SO_2 concentration (both using above background values) is $8.9 \mu\text{m}^3\text{cm}^{-1} \text{hr}^{-1} \text{ppm}^{-1}$. This ratio has been used as an indicator of the gas-to-particle rate. Whitby (at Labadie) (22) reported an average of 57.2 ± 40 and Hegg and Hobbs (5) reported an average of 58.4 ± 102 for several of their studies; both averages have very large standard deviations.

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